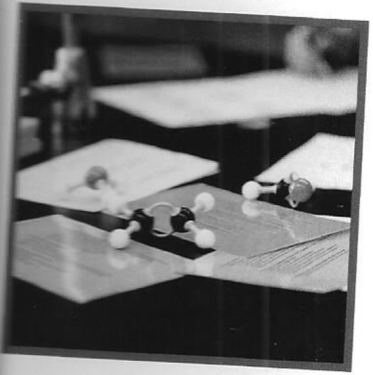
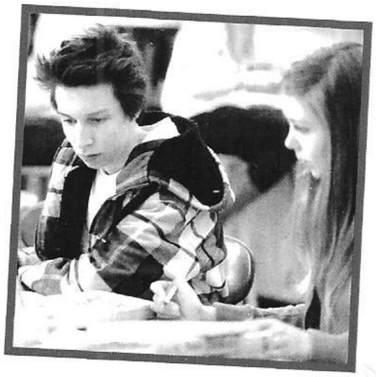
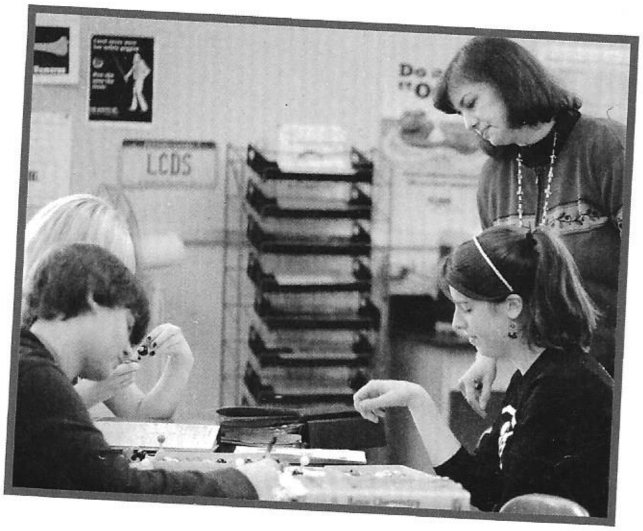
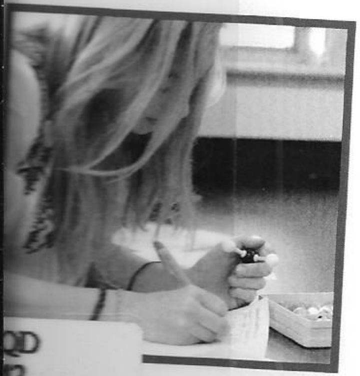
POGIL™

Activities for AP* Chemistry









Laura Trout
Editor

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Activities for AP* Chemistry

Developed through the High School POGIL Initiative
Laura Trout, Editor-in-Chief

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Preface

This activity collection is an extension of the High School POGIL Initiative (HSPI), a three-year effort (2008-2011) to bring student-centered, guided-inquiry instruction to secondary level classrooms, based on the principles of Process Oriented Guided-Inquiry Learning (POGIL), a group-learning, research-based instructional strategy.

In a POGIL classroom, students work cooperatively in self-managed teams, using carfelly designed materials, such as the activities included in this collection, that guide them to construct new understandings while they simultaneously develop key process skills, including critical thinking, problem solving, and collaboration.

The POGIL Project (www.pogil.org) is an independent not-for-profit organization, housed at Franklin & Marshall College, whose mission is to connect and support educators from all disciplines interested in implementing, improving, and studying student-centered pedagogies and leaning environments. The POGIL Project has received more than $6 million in National Science Foundation (NSF) funding, $600,000 from the U.S. Department of Education, and $564,000 from private foundations.

Since its inception in 2003, The POGIL Project has grown beyond its initial target audience of science faculty at higher education institutions to include more than 1,500 practitioners in its network of implementers at colleges, university, and high schools in every state in the country. The POGIL Project has presented more than 350 workshops and events, which have been attended by more than 7,500 people.

These activities contain several features which make them easy to use. Each activity has a "Teacher Resources" section, where you will find clear learning objectives, prerequisites, assessment questions, and teacher tips about facilitating the lesson. Within the activity, you will find stop signs at strategic points. These indicate good places for reporting out as a whole class or using other methods to check for understanding before moving on. Key icons mark questions containing important content which directly relate to the learning objectives. Each of these activities also includes optional extension questions. These questions go beyond the learning objectives stated in the teacher resources, and therefor truly are optional. They help to differentiate the learning experience in your classroom, and keep faster moving groups occupied while others finish the required questions.

Understanding effective classroom implementation is essential for a successful experience when using POGIL materials with students. We encourage everyone who plans to incorporate these activities into their classes to learn more about effective classroom strategies for student-centered work. The POGIL Project offers a wide array of training opportunities, including: webinars, presentations at regional and national conferences (ACS, NABT, BCCE, ChemEd, NSTA), introductory workshops, multiday regional workshops each summer, and custom workshops as requested.

Also available through The POGIL Project Web site is our interactive Implementation Guide. This web-based guide includes resources and materials to help you and your students get the maximum instructional benefits from incorporating these activities into your classroom.

Visit www.pogil.org for more information about The POGIL Project, to access the Implementation Guide, to see our events schedule and registration information, to request a workshop to be held at your institution or to make a donation to The Project.

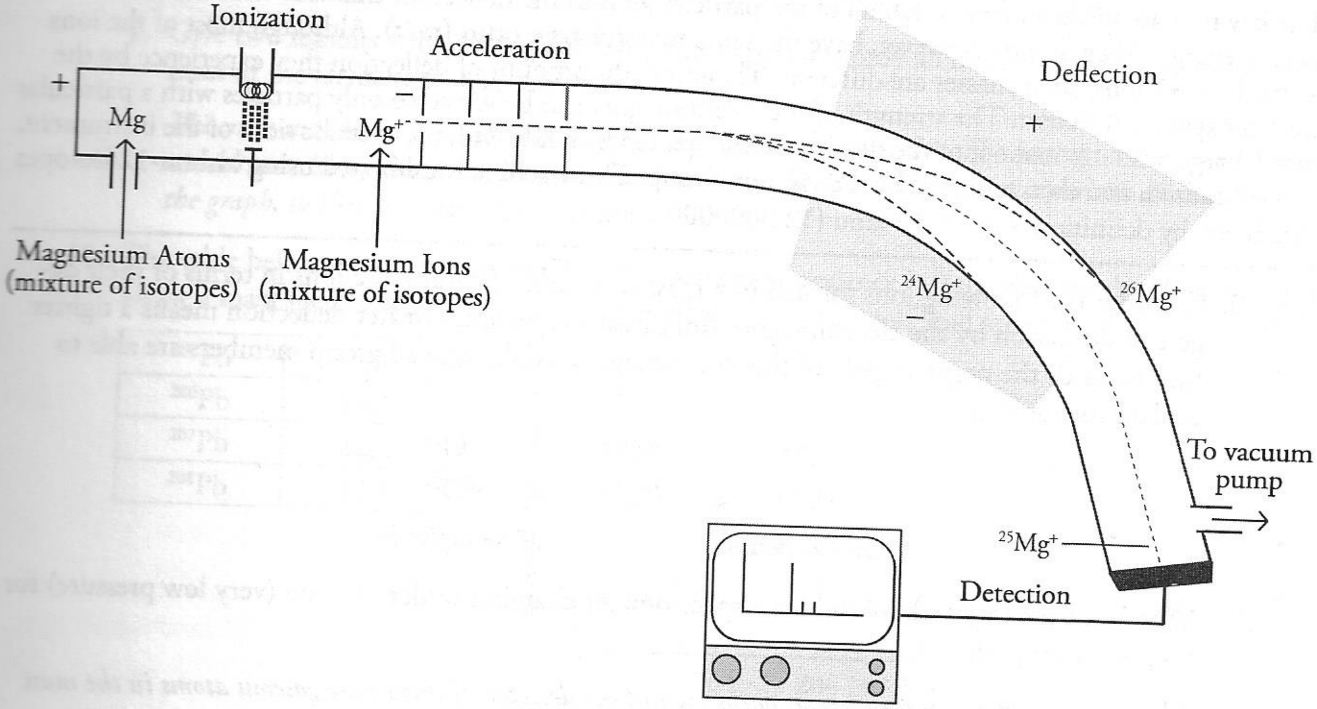
Mass Spectroscopy

How do we know isotopes exist?

Why?

When John Dalton proposed the first formal atomic theory, he stated "Atoms of the same element are identical." Today we know that is not true—many elements contain several different isotopes, or atoms that differ in mass. Mass spectroscopy is the principle technique used to study isotopes. It is used to both "count" and "weigh" atoms in a sample, just not in the traditional sense.

Model 1 – Sorting by Mass



1. According to Model 1 what four processes occur inside a mass spectrometer?

   Ionization, acceleration, deflection, and detection.

2. Consider where the sample is introduced into the mass spectrometer in Model 1. Which one of the four processes from Question 1 is the first process?

   Ionization

3. Match the four processes from Question 1 to the following descriptions.

Detection	Ions collide with a metal plate. Electrons are transferred from the metal to the ion, producing a current and thus a signal to a computer.
Deflection	Ions are attracted to the negative side of an electromagnetic field causing separation of the mixture based on mass and charge.
Ionization	Electrons are knocked off sample particles to form (mostly) +1 ions.
Acceleration	Ions move through a series of charged plates to form a narrow beam of high speed particles with equal kinetic energy.

4. When a sample is injected into the mass spectrometer, do the atoms or molecules turn into positive or negative ions? Justify your answer with at least two pieces of evidence from Model 1.

   The ions formed are positive because they are attracted to the negative terminals in the ionization chamber and of the electromagnetic field.

5. According to Model 1, what causes the sample mixture to become separated?

   The mass of the ion changes the amount of deflection by the electromagnetic field. Heavier ions are not deflected as much as lighter ions.

Read This!

The key to mass spectrometry is that all of the particles go into the deflection chamber with the same kinetic energy. They do not, however, have the same **mass/charge ratio (m/z)**. Although most of the ions formed are +1 ions, their masses are different. Therefore, the amount of deflection they experience by the electromagnet is different. The strength of the electromagnet can be varied so only particles with a particular mass/charge ratio can make it to the detector. Other particles collide with the metallic sides of the instrument, are neutralized, and then removed by the vacuum pump. The machine is calibrated using carbon-12 isotopes which are, by definition, exactly 12 amu (12.0000000…amu).

6. Consider the following ions formed in a mass spectrometer. Rank the ions in terms of their degree of deflection by the electromagnet from least to greatest. Greater deflection means a tighter turn towards the negative pole of the electromagnet. Make sure all group members are able to explain the ranking.

   $^{19}F^{1+}$ $^{16}O^{1+}$ $^{17}O^{1+}$

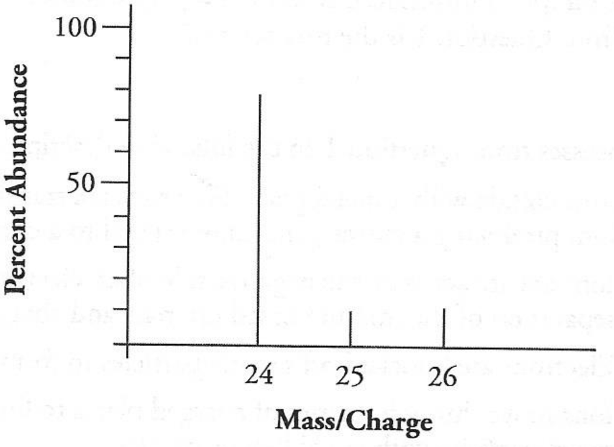
   $^{19}F^{1+} < {}^{17}O^{1+} < {}^{16}O^{1+}$

   Least deflection *More deflection*

7. Why is it necessary to have the mass spectrometer chamber under vacuum (very low pressure) for it to work properly?

   The ions must travel in continuous paths toward the detector. If there were gaseous atoms in the mass spectrometer chamber, they might impede the travel of the ions in the sample.

Model 2 – A Mass Spectrum



8. Model 2 is the mass spectrum that resulted from the experiment in Model 1.

   a. What is the mass number of the most common isotope of magnesium?

   24

   b. What is the percent abundance of the most common isotope of magnesium?

   80%

9. The average atomic mass of an element can be estimated from data on a mass spectrum.

   a. Calculate the average atomic mass of magnesium using data from Model 2. *Hint:* You will not get the correct answer if you add 24, 25 and 26 and divide by 3.

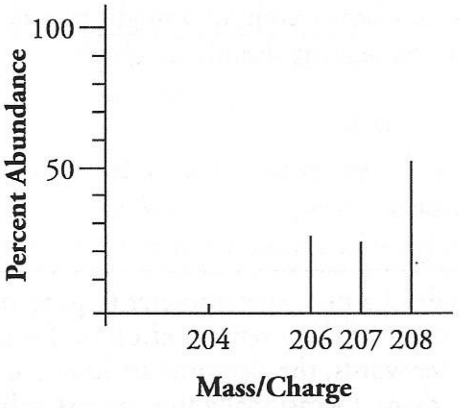
   Average atomic mass $= (24)(0.80) + (25)(0.10) + (26)(0.10) = 24.3$ *amu*

   b. Give two reasons why your calculated value in part *a* is only an estimate of the average atomic mass of the element magnesium.

   The mass number is not the same as the atomic mass of the isotopes. The average atomic mass would most likely not be an integral number. It is difficult to read the exact percent abundance on the graph, so they are estimated.

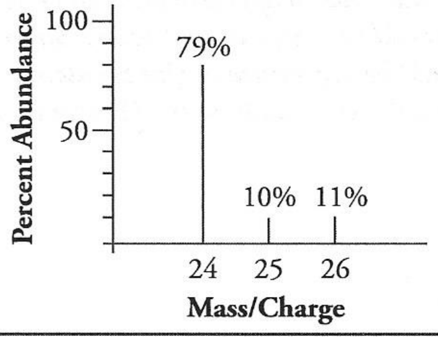
10. The table below provides mass number and percent abundance information for the element lead. Draw a mass spectrum for lead. (You can assume only +1 ions of lead are formed.)

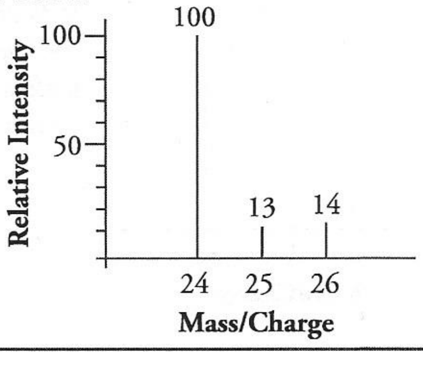
^{204}Pb	1.4%
^{206}Pb	24.1
^{207}Pb	22.1
^{208}Pb	52.4



Read This!

The mass spectra you have been looking at in this activity used percent abundance on the *y*-axis. Typically, however, the spectra use relative intensity. The ions from the sample are sorted by mass/charge ratio by the mass spectrometer. The ion that hits the detector most often is assigned a relative intensity of 100. The other ions are given proportional relative intensities based on their abundance in the sample. An example of magnesium's mass spectrum shown both ways is given below.





11. Consider the two mass spectra in the *Read This!* box.

    a. The sum of all percent abundances for magnesium is equal to 100. Explain why this is reasonable.

    If all of the isotopes are accounted for, you must have 100% of the atoms.

    b. The sum of all relative intensities for magnesium does not equal 100. Explain why this is reasonable.

    Since the tallest peak is assigned 100, the total of all peaks will be greater than 100 unless there is only one isotope (one peak).

12. Imagine that the relative intensities on the mass spectra in the *Read This!* box represent the number of particles in a sample.

    a. Theoretically, how many magnesium ions were detected by the mass spectrometer?

    $100 + 13 + 14 = 127$

    b. What percentage of the ions were ^{24}Mg ions? Show mathematical work to support your answer.

    $$\frac{100}{127} = 78.7\% \approx 79\%$$

    c. Show mathematically how a computer might translate the 13 peak in the relative intensity graph to 10% for the percent abundance graph.

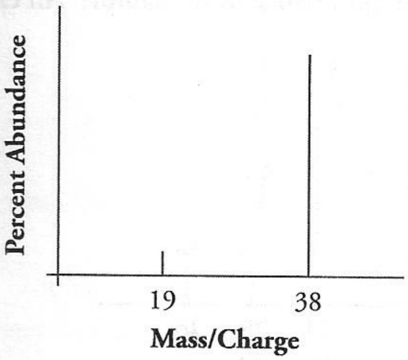
    $$\frac{13}{127} = 10.2\% \approx 10\%$$

STOP

Read This!

The process of ionization inside of a mass spectrometer is quite violent. There are several methods of ionization used in industry, but many of them remove electrons from the atoms or molecules by high energy particle bombardment. In other words, the electrons are knocked off the atoms or molecules by high speed particles colliding with them. Occasionally this process will break apart a molecule. This is called **fragmentation**. The pieces are analyzed by the mass spectrometer along with the whole molecules.

13. The following information was gathered by mass spectroscopy for the element fluorine. Fluorine has only one natural isotope, but it does form diatomic molecules naturally. Propose an explanation for the two lines on fluorine's mass spectrum.



The mass number for atomic fluorine is 19. A diatomic molecule of fluorine would have an approximate mass of 38. Since most of the fluorine would be diatomic, that peak is larger. Some of the molecules would be fragmented to give the atomic peak at 19. This happens only occasionally, so the 19 peak is much smaller.

14. The element chlorine has two natural isotopes: $^{35}\mathrm{Cl}$ (76% abundance) and $^{37}\mathrm{Cl}$ (24% abundance). The mass spectrum of chlorine has five lines.

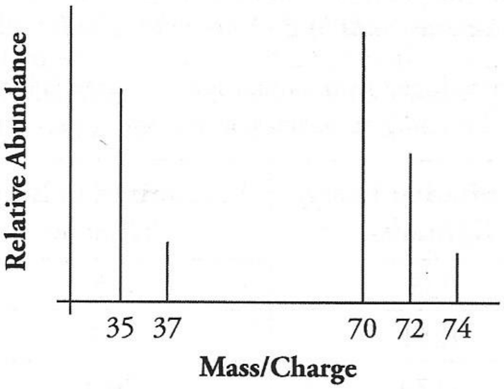
   a. Three of the lines in the mass spectrum are from diatomic molecules of chlorine. List the three possible combinations of the two isotopes and their total mass number.

   $^{35}Cl_2^+ = 70$ $^{37}Cl_2^+ = 74$ $^{35}Cl{-}^{37}Cl^+ = 72$

   b. Explain the remaining two lines in the spectrum.

   The other lines would be from the fragments (single atoms) of chlorine: $^{35}Cl^+$ *and* $^{37}Cl^+$.

   c. Draw a mass spectrum that would result from diatomic chlorine. Include the mass/charge number and estimate the relative abundance of each ion. (Assume only +1 ions are formed.) Although the heights of the peaks are difficult to predict you should be able to determine which will be taller or shorter based on the abundance of each chlorine isotope.



Answers will vary. Students should be able to show understanding by including both the single atom peaks and the molecular peaks. The heights of the peaks are more difficult to predict, but there should be some indication that the ^{35}Cl *is more common, and therefore those peaks will be higher.*

Extension Questions

Model 3 – Successive Ionization Energies

1st Ionization	$Mg(g) + \text{energy} \rightarrow Mg^{1+}(g) + e^-$
2nd Ionization	$Mg^+(g) + \text{energy} \rightarrow Mg^{2+}(g) + e^-$

15. List two ways that the first ionization and second ionization of an atom are similar.

Answer may include: both require energy, both remove one electron, both result in a positive ion being formed, and both remove electrons from gaseous particles.

16. List two ways that the first ionization and second ionization of an atom are different.

First ionization removes an electron from a neutral atom while second ionization removes an electron from a 1^+ ion. Second ionization results in a 2^+ ion while first ionization results in a 1^+ ion.

17. Occasionally a particle introduced into a mass spectrometer is ionized twice, causing a 2^+ ion to be formed. Consider the 1st and 2nd ionization energies of several atoms in the table below.

Element	1st Ionization Energy (kJ/mole)	2nd Ionization Energy (kJ/mole)
Magnesium	738	1451
Chlorine	1251	2298
Xenon	1170	2046
Oxygen	1314	3388

a. How do 1st ionization and 2nd ionization energies usually compare for an atom?

The second ionization energies are always higher than the 1st ionization energies.

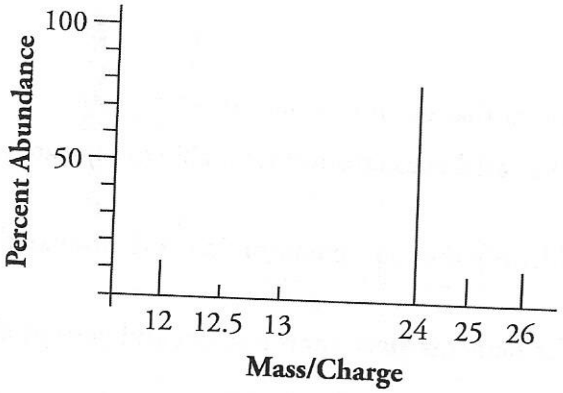
b. Propose a reason why very few 2^+ ions are formed in a mass spectrometer.

Since more energy is required to remove the second electron, this process happens successfully less often.

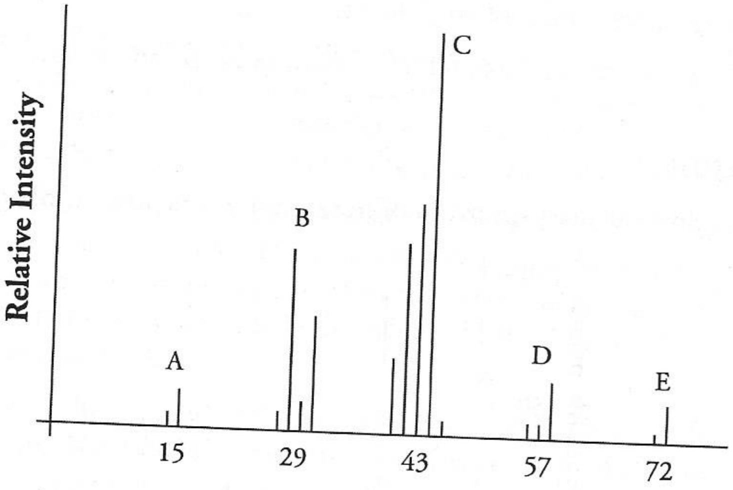
c. If 2^+ ions of magnesium were formed in the mass spectrometer chamber illustrated in Model 1, would they be deflected more or less than the 1^+ ions by the electromagnet?

The 2^+ ions would be attracted to the negative pole of the magnet more than the 1^+ ions, so there would be more deflection.

18. What would the mass spectrum of magnesium look like if a small portion of atoms were ionized to 2^+ ions?



19. Mass spectroscopy is also used to study large organic molecules. When a sample of a pure compound is analyzed in the instrument, some of the molecules get ionized whole (molecular ions), while some are fragmented and ionized. The fragmentation occurs in predictable patterns allowing scientists to propose chemical structures for unknown substances. Consider the mass spectrum of pentane ($CH_3CH_2CH_2CH_2CH_3$) shown below.



a. Match the molecular ion and fragment ions below to each of the lettered peak clusters in the mass spectrum.

$CH_3CH_2CH_2CH_2CH_3^+$	*E*
$CH_3CH_2CH_2CH_2^+$	*D*
$CH_3CH_2CH_2^+$	*C*
$CH_3CH_2^+$	*B*
CH_3^+	*A*

b. Peak cluster A has a small peak at 14. What may have fallen of the CH_3^+ ion to form this peak?

Most likely a hydrogen atom fell off in the fragmentation to form a CH_2^+ ion.

Teacher Resources – Mass Spectroscopy

Learning Objectives

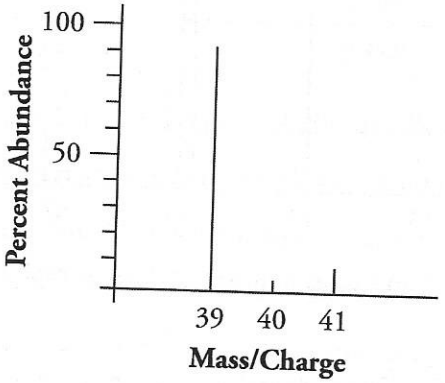
1. Describe the four processes that occur in a mass spectrometer.
2. Explain how the use of a variable electromagnet is able to separate particles in the sample by their mass/charge ratio.
3. Read mass spectra to identify the most common ion and estimate the average atomic mass of an element.
4. Predict mass spectra for elements given mass number and percent abundance information.

Prerequisites

1. Students should understand that most elements consist of a mixture of isotopes and that these isotopes are identified by their mass number.
2. Students should be able to use percent abundance and mass number (or atomic mass) data to calculate the average atomic mass of an element.
3. Students should have a basic understanding of the process of ionization.

Assessment Questions

1. Is the spectrum below the mass spectrum of potassium or calcium? Justify your reasoning.



2. Predict the mass spectrum for a sample of copper given the following data.

   ^{63}Cu 69.17%

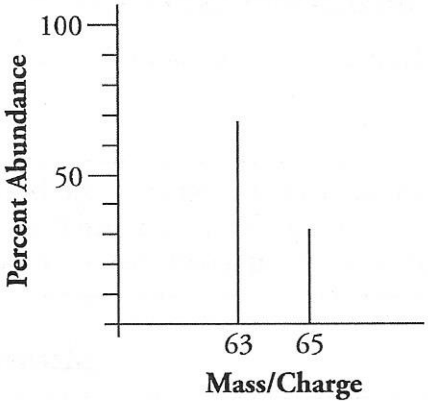
   ^{65}Cu 30.83%

3. Describe the processes that occur inside a mass spectrometer to analyze an elemental sample.

Assessment Target Responses

1. *The mass spectrum must be for potassium. The average atomic mass for potassium is 39.098 while that of calcium is 40.078. Since the largest peak is at mass number 39, it follows that the average atomic mass will be near 39 amu. The peak at mass number 40 is very small, so it is mathematically impossible to have an average around 40.*

2.



3. *First the atoms or molecules must be ionized, and then they are accelerated by charged plates so that all particles have the same kinetic energy. The charged particles pass through a magnetic field that deflects them at different amounts based on the mass/charge ratio. Finally, the charged particles hit the detection plate causing a current and registering a signal in the computer.*

Teacher Tips

- One of the most difficult concepts for students concerning isotopes is calculating the average atomic mass. Students typically will add each isotope's mass number (or atomic mass) and divide by the number of isotopes. This assumes that each isotope is equally abundant. You may want to remind students how to calculate a weighted average before they start this activity.
- This activity does not go into the details of how ionization occurs in the mass spectrometer because there are a variety of ways this is accomplished in today's machines. The most common is electrospray ionization where the particles are bombarded by high energy electrons that knock electrons off the particles. Other methods include chemical ionization and matrix assisted laser desorption ionization (MALDI).
- It may be useful to show a model of a mass spectrometer. In the Flinn Scientific *Mass Spectrometer Model Kit*, Catalog No. AP8717, students use different sized metallic and nonmetallic spheres to visualize the deflection that occurs in the machine.
- See the "Isotopes" and "Average Atomic Mass" activities in *POGIL Activities for High School Chemistry* for a great introduction to isotopes if students have not seen this material before.

Alignment with AP Chemistry Framework

- **Essential Knowledge 1.D.2:** An early model of the atom stated that all atoms of an element are identical. Mass spectrometry data demonstrate evidence that contradicts this early model.

  Learning Objective 1.14 The student is able to use data from mass spectrometry to identify the elements and the masses of individual atoms of a specific element.

Empirical Formulas

How can the chemical formulas of a compound be determined?

Why?

Scientists use chemical formulas as a shorthand method of communicating with each other about the make-up and structure of compounds. There are several types of formulas that are used to convey different types of information. This activity will compare two types of useful formulas.

Model 1 – Empirical Formula

Compound Name	Molecular Formula	Ratio of Carbon Atoms to Hydrogen Atoms	Lowest Whole Number Ratio of Carbon Atoms to Hydrogen Atoms	Empirical Formula
Methane	CH_4	1:4	1:4	CH_4
Ethene (ethylene)	C_2H_4	2:4	1:2	CH_2
Propene	C_3H_6	*3:6*	*1:2*	CH_2
Ethyne (acetylene)	C_2H_2	2:2	1:1	CH
Benzene	C_6H_6	*6:6*	*1:1*	CH
1,3-butadiene	C_4H_6	*4:6*	*2:3*	C_2H_3
Propane	C_3H_8	*3:8*	*3:8*	C_3H_8

1. Consider the information in Model 1. How are the columns "ratio of carbon atoms to hydrogen atoms" and "lowest whole number ratio of carbon atoms to hydrogen atoms" related?

   The "lowest whole number ratio" column is the same ratio as the "carbon to hydrogen" column, but reduced.

2. Complete the table in Model 1 by filling in all of the blank spaces.

   See Model 1.

3. Which set of ratios in Model 1 is most closely related to the empirical formulas of the compounds—the ratio of the carbon to hydrogen atoms or the lowest whole number ratio of carbon atoms to hydrogen atoms?

   The "lowest whole number ratio" column relates best to the empirical formula.

4. According to Model 1, is the empirical formula for a compound always different from the molecular formula of a compound? If no, describe a case when these two formulas would be the same.

   No. The empirical formula and molecular formula are the same when the molecular formula cannot be reduced. For example, CH_4 *and* C_3H_8 *are already in their lowest whole number ratio, so the empirical formula is the same as the molecular formula.*

5. Imagine you are helping a friend who missed class today. Briefly explain to your friend how to write the empirical formula for a compound when given the molecular formula.

   Take the ratio of atoms from the molecular formula and reduce it to the lowest whole number ratio. The empirical formula should display the lowest whole number ratio of atoms.

6. Could a specific compound be identified uniquely by its empirical formula? Justify your answer with specific examples from Model 1.

   No, several compounds might have the same empirical formula. For example, ethyne and benzene both have an empirical formula of CH.

7. Write the empirical formulas for each of the following compounds.

C_5H_{10}	C_4H_{10}	N_2O_5	P_4O_{10}	SO_2
CH_2	C_2H_5	N_2O_5	P_2O_5	SO_2

STOP

Model 2 – Percent Composition

Compound Name	Molecular Formula	Moles Carbon in 1 Mole of Compound	Moles Hydrogen in 1 Mole of Compound	Grams Carbon in 1 Mole of Compound	Grams Hydrogen in 1 Mole of Compound	Carbon % Mass	Hydrogen % Mass
Methane	CH_4	1.00 mole	4.00 moles	12.00 g	4.00 g	75.0%	25.0%
Ethene (ethylene)	C_2H_4	2.00 moles	4.00 moles	24.00 g	4.00 g	85.7%	14.3%
Propene	C_3H_6	3.00 moles	6.00 moles	36.00 g	6.00 g	85.7%	14.3%
Ethyne (acetylene)	C_2H_2	*2.00 moles*	*2.00 moles*	*24.00 g*	*2.00 g*	*92.3%*	*7.7%*
Benzene	C_6H_6	*6.00 moles*	*6.00 moles*	*72.00 g*	*6.00 g*	*92.3%*	*7.7%*
1,3-butadiene	C_4H_6	*4.00 moles*	*6.00 moles*	*48.00 g*	*6.00 g*	*88.9%*	*11.1%*
Propane	C_3H_8	*3.00 moles*	*8.00 moles*	*36.00 g*	*8.00 g*	*81.8%*	*18.2%*

8. Consider the data in Model 2. Discuss as a group how the values were obtained in each column, then divide the work for completing the remaining four compounds. Show your work below.

   For methane:

$$1 \text{ mole C} \times \frac{12.00\text{ g}}{1\text{ mole}} = 12.00\text{ g}$$

$$4 \text{ moles H} \times \frac{1.00\text{ g}}{1\text{ mole}} = 4.00\text{ g}$$

$$\text{total mass} = 12.00\text{ g} + 4.00\text{ g} = 16.00\text{ g}$$

$$\%\text{ carbon} = \frac{12.00\text{ g}}{16.00\text{ g}} \times 100 = 75.00\%$$

$$\%\text{ hydrogen} = \frac{4.00\text{ g}}{16.00\text{ g}} \times 100 = 25.0\%$$

9. Refer to Model 2. What do you notice about the percent composition of compounds with the same empirical formulas?

When compounds have the same empirical formula, they also have the same percent composition.

10. Could a specific compound be identified uniquely by its percent composition? Justify your answer with specific examples from Model 2.

No, more than one compound can have the same percent composition. For example, in Model 2, ethene and propene have the same percent composition.

11. Use the data in Model 2 to perform the following calculations by first discussing as a group how the calculations would be done, and then dividing the work among group members. List your answers in the table below. Several of the calculations have been done for you as examples.

   a. Calculate the lowest whole number ratio of moles of carbon in 1 mole of compound to moles of hydrogen in 1 mole of compound.

   b. Calculate the lowest whole number ratio of mass of carbon in 1 mole of compound to mass of hydrogen atoms in 1 mole of compound.

   c. Calculate the lowest whole number ratio of carbon percent mass to hydrogen percent mass for each compound. *Hint:* If the lowest whole number ratio is not clear by inspection, divide both values by the lesser of the two numbers.

Molecular Formula	**Empirical Formula**	**Lowest Ratio of Moles C : Moles H**	**Lowest Ratio of Mass C : Mass H**	**Lowest Ratio of % C : % H**
CH_4	CH_4	1 : 4	3 : 1	3 : 1
C_2H_4	CH_2	1 : 2	6 : 1	6 : 1
C_3H_6	CH_2	1 : 2	6 : 1	6 : 1
C_2H_2	*CH*	*1 : 1*	*12 : 1*	*12 : 1*
C_6H_6	*CH*	*1 : 1*	*12 : 1*	*12 : 1*
C_4H_6	C_2H_3	*2 : 3*	*8 : 1*	*8 : 1*
C_3H_8	C_3H_8	*3 : 8*	*9 : 2*	*9 : 2*

   d. Which of the ratios in the table above correlates best to the empirical formula of the compound?

   The lowest ratio of moles C : moles H gives the empirical formula.

12. Compare the ratio of mass carbon to mass hydrogen to the ratio of percent mass carbon to percent mass hydrogen for any compound in Model 2 (the table in Question 11 might be helpful as well). Do they match?

For methane: 12.00 g : 4.00 g reduces to 3 : 1
75% : 25% reduces to 3 : 1

Yes, the ratio of masses matches the ratio of percents.

Read This!

When chemists are working with a new or unknown compound, one method they can use to determine the chemical formula of the substance is to determine the percent composition. There are several methods for chemically breaking down a compound and finding the relative masses of the elements in the substance. These data are then used to determine the empirical formula of the substance. Although this does not provide the molecular formula, it is a step in the right direction.

13. Consider the four samples of methane below. According to Model 2, the percent composition for methane is 75.0% carbon and 25.0% hydrogen. Use this information to fill in the table below. Divide the work among group members. Show your work for each calculation.

Total Mass of Methane Sample	100.0 g	72.0 g	12.0 g	10.0 g
Grams of Carbon Atoms	*75.00 g*	*54.0 g*	*9.00 g*	*7.50 g*
Moles of Carbon Atoms	*6.250 moles*	*4.50 moles*	*0.750 mole*	*0.625 mole*
Grams of Hydrogen Atoms	*25.00 g*	*18.0 g*	*3.00 g*	*2.50 g*
Moles of Hydrogen Atoms	*25.00 moles*	*18.0 moles*	*3.00 moles*	*2.50 moles*
Lowest Whole Number Ratio of Moles C : Moles H	*1 : 4*	*1 : 4*	*1 : 4*	*1 : 4*

$$72.0\ g\ sample \times 0.75\ carbon = 54.0\ g\ carbon \qquad 54.0\ g \times \frac{1\ mole}{12.0\ g} = 4.50\ moles\ carbon$$

$$72.0\ g\ sample \times 0.25\ hydrogen = 18.0\ g\ hydrogen \qquad 18.0\ g \times \frac{1\ mole}{1.00\ g} = 18.0\ moles\ hydrogen$$

$$\frac{18.0\ moles}{4.50\ moles} = 4.00$$

C to H ratio → 1 : 4

14. Refer to your work in Question 13.
    a. Can the empirical formula of a compound be derived mathematically from percent composition data? Justify your answer.

       Yes, percent composition data can be used to derive the empirical formula of a compound. The percent data can be used to calculate the moles of each element in the compound, and the ratio between them.

    b. Would you need to know the mass of the sample when determining a compound's empirical formula from percent composition data?

       No, the mass of the sample does not matter. Any starting mass could be used.

STOP

15. List the steps needed to find the empirical formula for a compound when given the percent composition.

    1) Assume a sample size—100.0 g or 10.0 g work nicely.

    2) Calculate the mass of each element in the sample by multiplying the sample size by the percent composition of each element.

    3) Convert the mass of each element to moles.

    4) Find the lowest whole number ratio of moles of atoms.

16. An unknown compound contains 50% sulfur and 50% oxygen. Determine the empirical formula of the compound. Show mathematical calculations to support your answer.

    Assume the sample of unknown compound is 10.0 g.

    The sample therefore contains 5.00 g of sulfur and 5.00 g of oxygen.

$$5.00\ \text{g sulfur} \times \frac{1\ \text{mole}}{32.066\ \text{g}} = 0.156\ \text{mole sulfur}$$

$$5.00\ \text{g oxygen} \times \frac{1\ \text{mole}}{15.999\ \text{g}} = 0.313\ \text{mole oxygen}$$

$$\frac{0.313\ \text{mole}}{0.156\ \text{mole}} = 2.00$$

Empirical formula is SO_2.

17. Explain why the empirical formula of the compound in Question 16 is not SO even though its percent composition is 50 : 50.

    Percent composition is a ratio of masses. The empirical formula, however, is a ratio of moles. Since the sulfur atoms are heavier than the oxygen atoms, the ratio of moles is not 1 : 1.

18. An unknown compound contains 43.6% phosphorus and 56.4% oxygen. Determine the empirical formula of the compound. Show mathematical calculations to support your answer.

    Assume the sample of unknown compound is 10.0 g.

    The sample therefore contains 4.36 g phosphorus and 5.64 g oxygen.

$$4.36\ \text{g phosphorus} \times \frac{1\ \text{mole}}{30.974\ \text{g}} = 0.141\ \text{mole phosphorus}$$

$$5.64\ \text{g oxygen} \times \frac{1\ \text{mole}}{15.999\ \text{g}} = 0.353\ \text{mole oxygen}$$

$$\frac{0.353\ \text{mole}}{0.141\ \text{mole}} = 2.50$$

Empirical formula is P_2O_5.

19. Do you know the molecular formula of either of the compounds in Questions 16 or 18? Explain your reasoning.

No, the molecular formula is still unknown. It could be any multiple of the calculated empirical formulas.

Read This!

The empirical formula of an unknown compound can be derived from percent composition data, but you still will not know which compound you have. You will, however, have narrowed down the possibilities. For example, if you know the empirical formula of a compound is C_2H_3, the molecular formula might be C_2H_3, C_4H_6, C_6H_9, C_8H_{12}, etc. In order to determine the molecular formula of a compound, you must know the compound's molar mass. This will allow you to determine which multiple of the empirical formula is the correct molecular formula.

20. The molar mass of the compound in Question 18 is 283.88 g/moles. Use complete sentences to explain how this information could be used to determine the molecular formula of the compound. *Hint:* This question is not asking you to simply determine the molecular formula.

The molecular formula must be some multiple of the empirical formula. Therefore, the molar mass of 283.88 g/mole must be a multiple of the mass of the empirical formula. First, add up the total mass of atoms in 1 mole of the empirical formula. Divide that value into the molar mass of the compound. The answer is the multiplier that must be used on the empirical formula to get the molecular formula.

21. Nicotine is a stimulant found in the tobacco plant. The percent composition is: 74.03% C, 8.70% H and 17.27% N.

a. Determine the empirical formula of nicotine.

Assume a 10.0 g sample.

$$7.403 \text{ g carbon} \times \frac{1 \text{ mole}}{12.01 \text{ g}} = 0.6164 \text{ mole}$$

$$0.870 \text{ g hydrogen} \times \frac{1 \text{ mole}}{1.008 \text{ g}} = 0.863 \text{ mole}$$

$$1.727 \text{ g nitrogen} \times \frac{1 \text{ mole}}{14.00 \text{ g}} = 0.1234 \text{ mole}$$

$$C:H:N \rightarrow \frac{1 \text{ mole}}{14.00 \text{ g}} : \frac{0.863}{0.1234} : \frac{0.1234}{0.1234} \rightarrow 5:7:1$$

C_5H_7N

b. The molar mass of nicotine is 163.23 g/mole. Using this information and your answer to part *a*, calculate the molecular formula of nicotine.

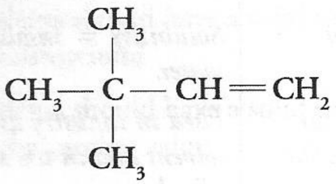
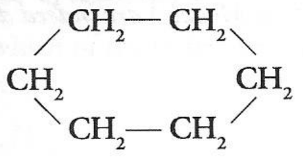
C_5H_7N *mw* = 81 g/mole

$$\frac{163.23}{81} = 2.0$$

Molecular formula $\rightarrow C_{10}H_{14}N_2$

Extension Questions

Model 3 – Isomers

Structural Formula	Molecular Formula	Empirical Formula
1-hexene $CH_3-CH_2\ CH_2\ CH_2\ CH=CH_2$	C_6H_{12}	CH_2
3,3-dimethyl-1-butene  $CH_3-C(CH_3)_2-CH=CH_2$	C_6H_{12}	CH_2
cyclohexane 	C_6H_{12}	CH_2

22. Determine the molecular formula and empirical formula for each of the compounds in Model 3.

    See Model 1.

23. In all cases, can a specific compound be identified uniquely by its molecular formula? Justify your answer with specific examples from Model 3.

    No, all three of the compounds in Model 3 have the same molecular formula.

24. The three substances in Model 3 are isomers. Write a definition for the term isomers.

    Substances with the same molecular formula, but different structural formulas.

25. What are the advantages and disadvantages of using structural formulas to represent a compound?

    The advantage is that it shows how atoms are bonded—their arrangement in space. This can provide some insight into their chemical and physical properties. It also makes it clear which substance you are using. The disadvantage is that it takes up a lot of space on the page and takes more time to draw.

26. Make a prediction. Do you think the isomers in Model 3 will have the same physical properties such as melting point, boiling point and solubility? Explain your reasoning.

    The compounds will have slightly different physical properties because these are based on intermolecular forces. Although all three isomers have the same mass, the arrangement of atoms is different. This will affect the strength of intermolecular forces, namely the London dispersion forces.

27. Make a prediction. Do you think the isomers in Model 3 will have the same chemical properties? Explain your reasoning.

    The 1-hexene and 3,3-dimethyl-1-butene might have the same chemical properties because they both contain a double bond and are structurally similar. However the cyclohexane does not contain a double bond and would likely have different chemical properties.

28. Find the three compounds in Model 3 in a textbook or on the Internet. Compare their physical and chemical properties. Are the three compounds really just the same substance or are they different substances? Justify your answer with information you find in your research.

1-Hexene	***3,3-Dimethyl-1-butene***	***Cyclohexane***
MP = −139.8 °C *BP = 63 °C* *Solubility = insoluble in water.* *Used as a monomer in the manufacture of high density polyethylene (HDPE) plastics.*	*MP = −115 °C* *BP = 41 °C* *Solubility = insoluble in water.* *Used as a building block for many pharmaceutical products.*	*MP = 6.47 °C* *BP = 80.74 °C* *Solubility = insoluble in water.* *Used in industry as a nonpolar solvent and in the manufacture of nylon.*

From the data above, students should conclude that the isomers in Model 3 are indeed different substances.

Teacher Resources – Empirical Formulas

Learning Objectives

1. Write the empirical formula for a compound when the molecular formula is provided.
2. Determine the empirical formula of a compound from percent composition data.
3. Discuss the limitations of an empirical formula in identifying a unique compound.

Prerequisites

1. Students should be able to determine the percent composition of a compound given the molecular formula.
2. Students should have a solid understanding of the mole and be able to calculate the molar mass of a compound.
3. Students should have a solid understanding of ratios and how to reduce a ratio to its lowest whole number value.

Assessment Questions

1. For which of the following compounds is the empirical formula and molecular formula the same?
   - *a.* C_6H_{14}
   - *b.* NO_2
   - *c.* $C_2H_4O_2$
   - *d.* S_2F_{10}
2. Benzoyl peroxide is a common medication for treating acne. It is also used to bleach hair and teeth. The molar mass of benzoyl peroxide is 242 g/mole. The percent composition is 69.4% carbon, 4.2% hydrogen and 26.4% oxygen. Determine the molecular formula of benzoyl peroxide.
3. Which type of formula, empirical or molecular, is more likely to uniquely identify a compound? Use examples to justify your answer.

Assessment Target Responses

1. *b*
2. *Assume a sample of 100.0 g. The sample would contain 69.4 g of carbon, 4.2 g of hydrogen and 26.4 g oxygen.*

$$69.4\ g\ carbon \times \frac{1\ mole}{12.011\ g} = 5.78\ moles\ carbon$$

$$4.2\ g\ hydrogen \times \frac{1\ mole}{1.0079\ g} = 4.2\ moles\ hydrogen$$

$$26.4\text{ g oxygen} \times \frac{1\text{ mole}}{15.999\text{ g}} = 1.65\text{ moles oxygen}$$

$$\frac{5.78}{1.65} : \frac{4.2}{1.65} : \frac{1.65}{1.65}$$

$3.5:2.5:1$

Multiply by 2

$7:5:2$

Empirical formula: $C_7H_5O_2$

Empirical formula mass $= 121$ *g/mole*

$$\frac{242\text{ g/mole}}{121\text{ g/mole}} = 2$$

Molecular formula: $C_{14}H_{10}O_4$

3. *The molecular formula communicates the actual number and types of atoms in the compound whereas the empirical formula communicates only the lowest ratio of atoms. For example, the empirical formula CH could represent the compounds* C_2H_2, C_6H_6.

Teacher Tip

- Students are not usually comfortable with ratios. This leads to confusion when working with percent composition and empirical formulas. For example, students will think they need to be given a sample mass with the percent composition data in order to find an empirical formula. Question 13 addresses this misconception by showing students that the starting mass of material does not matter. The ratio of moles will always reduce to the same ratio.

Alignment with AP Chemistry Framework

- **Essential Knowledge 1.A.2:** Chemical analysis provides a method for determining the relative number of atoms in a substance, which can be used to identify the substance or determine its purity.

  Learning Objective 1.2 The student is able to select and apply mathematical routines to mass data to identify or infer the composition of pure substances and/or mixtures.

Combustion Analysis

How can burning a substance help determine the substance's chemical formula?

Why?

Scientists have many techniques to help them determine the chemical formula or structure of an unknown compound. One commonly used technique when working with carbon-containing compounds is combustion analysis. Any compound containing carbon and hydrogen will burn. With an ample oxygen supply, the products of the combustion will be carbon dioxide and water. Analyzing the mass of CO_2 and H_2O that are produced allows chemists to determine the ratios of elements in the compound.

Model 1 – Combustion Reactions

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$C_2H_6 + \tfrac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

1. According to Model 1, what reactant is always required for combustion?

   Oxygen is always required for combustion.

2. Balance the reactions in Model 1 while keeping the hydrocarbon coefficient a "1." This may require the use of fractions in other places.

   See Model 1.

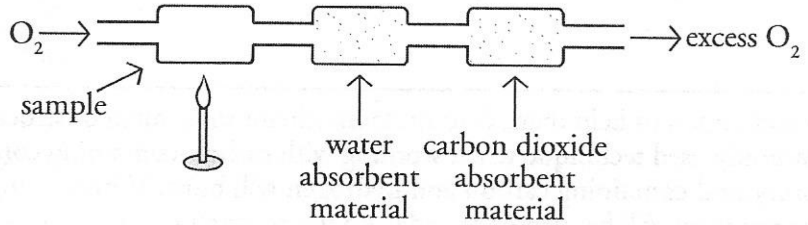
3. How is the coefficient of CO_2 in the chemical reactions in Model 1 related to the chemical formula of the hydrocarbon being analyzed?

   The coefficient of CO_2 is the same as the subscript on the carbon atoms in the hydrocarbon.

4. How is the coefficient of the H_2O in the chemical reactions in Model 1 related to the chemical formula of the hydrocarbon being analyzed?

   The coefficient of H_2O is half the subscript on the hydrogen in the hydrocarbon.

Read This!



In a combustion analysis experiment, a hydrocarbon sample is heated in a stream of oxygen gas. As the sample burns, water and carbon dioxide is pushed through a series of chambers with materials that absorb each of the respective products. The chambers are each weighed before and after the combustion to determine the mass of each product.

Model 2 – Combustion Analysis of C_xH_y Unknowns

10.00-g Sample	Mass of CO_2 Produced	Moles of CO_2	Moles of Carbon Atoms	Mass of H_2O Produced	Moles of H_2O	Moles of Hydrogen Atoms	Sample's Empirical Formula	Total Mass of C and H Atoms
1	27.42 g	*0.623*	*0.623*	22.46 g	*1.247*	*2.493*	CH_4	*10.00 g*
2	29.26 g	*0.665*	*0.665*	17.97 g	*0.997*	*1.994*	CH_3	*10.00 g*

30.00-g Sample	Mass of CO_2 Produced	Moles of CO_2	Moles of Carbon Atoms	Mass of H_2O Produced	Moles of H_2O	Moles of Hydrogen Atoms	Sample's Empirical Formula	Total Mass of C and H Atoms
3	94.11 g	*2.139*	*2.139*	38.53 g	*2.139*	*4.277*	CH_2	*30.00 g*
4	89.80 g	*2.041*	*2.041*	49.03 g	*2.721*	*5.442*	C_3H_8	*30.00 g*

5. Discuss with your group how the data in Model 2 could be used to calculate the following quantities:

Moles of CO_2	Moles of C atoms
Moles of H_2O	Moles of H atoms

Divide the work among group members to complete those four columns in Model 2. Show work for your calculations below.

$$27.42\ g\ CO_2 \times \frac{1\ mole}{44.01\ g} = 0.6232\ mole\ CO_2 \rightarrow 0.6232\ mole\ C\ atoms$$

$$22.46\ g\ H_2O \times \frac{1\ mole}{18.016\ g} = 1.247\ moles\ H_2O \rightarrow 2.493\ moles\ H\ atoms$$

6. Discuss with your group how the data from Model 2 could be used to find the lowest whole number ratio between carbon and hydrogen atoms. This will give you the empirical formulas of the sample substances. Fill in the last column of Model 2.

   $0.6232 \text{ mole C} : 2.493 \text{ mole H} \rightarrow 1:4 \rightarrow CH_4$

7. Did you need balanced chemical combustion equations to find the empirical formulas of the unknowns in Model 2?

   No, balanced chemical equations were not needed.

8. Did you need to know the mass of the samples to find the empirical formulas of the unknowns in Model 2?

   No, the mass of the samples was not needed.

9. What other information would you need to determine the molecular formulas?

   To find the molecular formulas, you would need to know the molar mass of the unknown compounds.

10. A 15.00-g sample of an unknown hydrocarbon is analyzed by combustion analysis. The sample produced 50.70 grams of carbon dioxide and 10.42 grams of water. Find the empirical formula of the unknown.

$$50.70 \text{ g } CO_2 \times \frac{1 \text{ mole}}{44.00 \text{ g}} = 1.153 \text{ moles } CO_2 \rightarrow 1.152 \text{ moles C atoms}$$

$$10.42 \text{ g } H_2O \times \frac{1 \text{ mole}}{18.016 \text{ g}} = 0.5783 \text{ mole } H_2O \rightarrow 1.157 \text{ moles H atoms}$$

$$1.152 \text{ mole C} : 1.157 \text{ mole H} \rightarrow 1:1 \rightarrow CH$$

11. Calculate the total mass of carbon atoms and hydrogen atoms for each sample in Model 2. Divide the work among group members. Create a new column in Model 2 for these data.

    a. How does the mass of carbon and hydrogen atoms compare to the mass of the original sample?

    The total mass of carbon and hydrogen atoms is equal to the original sample mass.

    b. Name the scientific law that justifies your answer to part *a*.

    The law of conservation of mass.

    c. Would part *a* be true if the original sample included atoms other than carbon and hydrogen? For example: C_2H_6O or $C_2H_5NH_2$. Justify your reasoning.

    If other elements were in the sample, the total mass of carbon and hydrogen atoms would be less than the mass of the sample. The nitrogen or oxygen atoms would be missing from the mass.

Read This!

When the combustion analysis unknown is a compound containing only carbon and hydrogen, all of the atoms in the sample end up in either the CO_2 or H_2O products. However, if the unknown contains other elements, like oxygen or nitrogen, those atoms might end up in the CO_2 and H_2O products (in the case of oxygen) or they might form other gases that move through the apparatus without being captured. Additionally, O atoms may come from the atmosphere as opposed to the combusting sample. Moles of these atoms cannot be calculated by stoichiometry directly. Instead, we must use the law of conservation of mass.

Model 3 – Combustion Analysis of $C_xH_yO_z$ Unknowns (10.00-g samples)

Sample	Mass of CO_2 Produced	Moles of Carbon Atoms	Mass of H_2O Produced	Moles of Hydrogen Atoms	Total Mass of C and H Atoms	Mass of O Atoms	Moles of O Atoms	Sample's Empirical Formula
1	19.10 g	*0.4341*	11.73 g	*1.302*	*6.526*	*3.47*	*0.217*	C_2H_6O
2	14.65 g	*0.3330*	6.00 g	*0.6661*	*4.6621*	*5.34*	*0.333*	CH_2O
3	21.96 g	*0.4991*	11.99 g	*1.331*	*7.325*	*2.67*	*0.167*	C_3H_8O
4	28.05 g	*0.6375*	5.74 g	*0.637*	*8.287*	*1.713*	*0.107*	C_6H_6O

12. Four unknown hydrocarbons containing oxygen were analyzed by combustion analysis. The samples were 10.00 g each. The results are shown in Model 3. Discuss with your group what calculations would need to be performed to complete the table in Model 3. Divide the work among group members. Show work for your calculations below.

$$19.10\ g\ CO_2 \times \frac{1\ mole}{44.00\ g} = 0.4341\ mole\ CO_2 \rightarrow 0.4341\ mole\ C\ atoms \rightarrow 5.214\ g\ carbon$$

$$11.73\ g\ H_2O \times \frac{1\ mole}{18.016\ g} = 0.6511\ mole\ H_2O \rightarrow 1.302\ moles\ H\ atoms \rightarrow 1.312\ g\ hydrogen$$

Total mass of C and H atoms = 6.526 g

Mass of O atoms = 10.00 g – 6.526 g = 3.47 g oxygen

$$3.47\ g\ O \times \frac{1\ mole}{15.999\ g} = 0.217\ mole\ O$$

$$\frac{0.4341\ mole}{0.217\ mole} : \frac{1.302\ moles}{0.217\ mole} : \frac{0.217\ mole}{0.217\ mole} \rightarrow 2C : 6H : 1O$$

13. Did you need balanced chemical combustion equations to find the empirical formula of your unknowns in Model 3?

No, a balanced chemical equation was not needed.

14. Did you need to know the mass of the samples to find the empirical formulas of your unknowns in Model 3?

Yes, the total mass of the samples was needed to find the mass of oxygen atoms.

15. A 15.00-g sample of a compound containing carbon, hydrogen and nitrogen is analyzed by combustion analysis. The sample produced 29.3 grams of carbon dioxide and 20.8 grams of water. Find the empirical formula of the unknown.

$$29.3\ g\ CO_2 \times \frac{1\ mole}{44.00\ g} = 0.666\ mole\ CO_2 \rightarrow 0.666\ mole\ C\ atoms \rightarrow 8.00\ g\ carbon$$

$$20.8\ g\ H_2O \times \frac{1\ mole}{18.016\ g} = 1.15\ moles\ H_2O \rightarrow 2.31\ moles\ H\ atoms \rightarrow 2.31\ g\ hydrogen$$

$$Total\ mass\ of\ C\ and\ H\ atoms = 10.31\ g$$

$$Mass\ of\ N\ atoms = 15.00\ g - 10.31\ g = 4.69\ g\ nitrogen$$

$$4.69\ g\ N \times \frac{1\ mole}{14.01\ g} = 0.335\ mole\ N$$

C_2H_7N

STOP

Extension Questions

16. It is critical in combustion analysis procedures that the sample be dry. Discuss what errors in data would occur if the sample contained moisture. How might this affect the final empirical formula?

    If the sample contains water impurities, then the water would evaporate from the sample during combustion and be absorbed by the water absorbent material. The mass of water would be too high, making the moles of hydrogen too high. The calculated empirical formula would have too many hydrogen atoms.

17. Discuss what errors in data would occur if the sample contained a carbon-based impurity. How might this affect the final empirical formula?

    If the sample contains a carbon impurity, then the carbon would burn just like the carbon in the sample, creating too much CO_2*. This would lead to calculating too many moles of carbon. The calculated empirical formula would have too many carbon atoms.*

18. Balance the general combustion equation below *using variables* for the missing coefficients.

$$C_xH_y + x + \frac{y}{4}O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

Teacher Resources – Combustion Analysis

Learning Objectives

1. Write a balanced chemical equation for the combustion of any hydrocarbon.
2. Find the empirical formula of an unknown substance from the mass of carbon dioxide and water resulting from combustion analysis.

Prerequisites

1. Students should be comfortable with stoichiometry calculations.
2. Students should appreciate the difference between the empirical formula and the molecular formula of a substance.
3. Students should have experience finding the empirical formula of an unknown from percent composition data or elemental mass data.

Assessment Questions

1. Which of the following chemical equations correctly represents the combustion of a hydrocarbon?
   a. $C_6H_{12}O_6 \rightarrow 6C + 6H_2O$
   b. $C_2H_4 + H_2 \rightarrow C_2H_6$
   c. $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
   d. $6CO_2 + 6H_2O \rightarrow 6O_2 + C_6H_{12}O_6$
2. Quinone, an oxygenated hydrocarbon, is a chemical used in the photography industry. When a 0.144-g sample is analyzed by combustion analysis, 0.352 g of carbon dioxide and 0.0480 g of water is produced. Find the empirical formula for quinone.
3. If an oxygen stream is not sufficient during a combustion analysis, the sample will undergo incomplete combustion, meaning not all of the carbon atoms are fully oxidized to CO_2 and other compounds, such as acetaldehyde and carbon monoxide, are produced. Assuming these substances are not absorbed during combustion analysis, describe the errors that would occur in determining the empirical formula if insufficient oxygen is used.

Assessment Target Responses

1. *c*
2. C_3H_2O
3. *The calculated empirical formula would have too few carbon atoms and too many oxygen atoms.*

Teacher Tip

- The most common mistake students make during combustion analysis calculations is to not consider the 2 : 1 ratio of hydrogen atoms in the water molecules. Analysis of Model 1 should help students understand why this is necessary.

Alignment with AP Chemistry Framework

- **Essential Knowledge 1.A.2:** Chemical analysis provides a method for determining the relative number of atoms in a substance, which can be used to identify the substance or determine its purity.

  Learning Objective 1.2 The student is able to select and apply mathematical routines to mass data to identify or infer the composition of pure substances and/or mixtures.

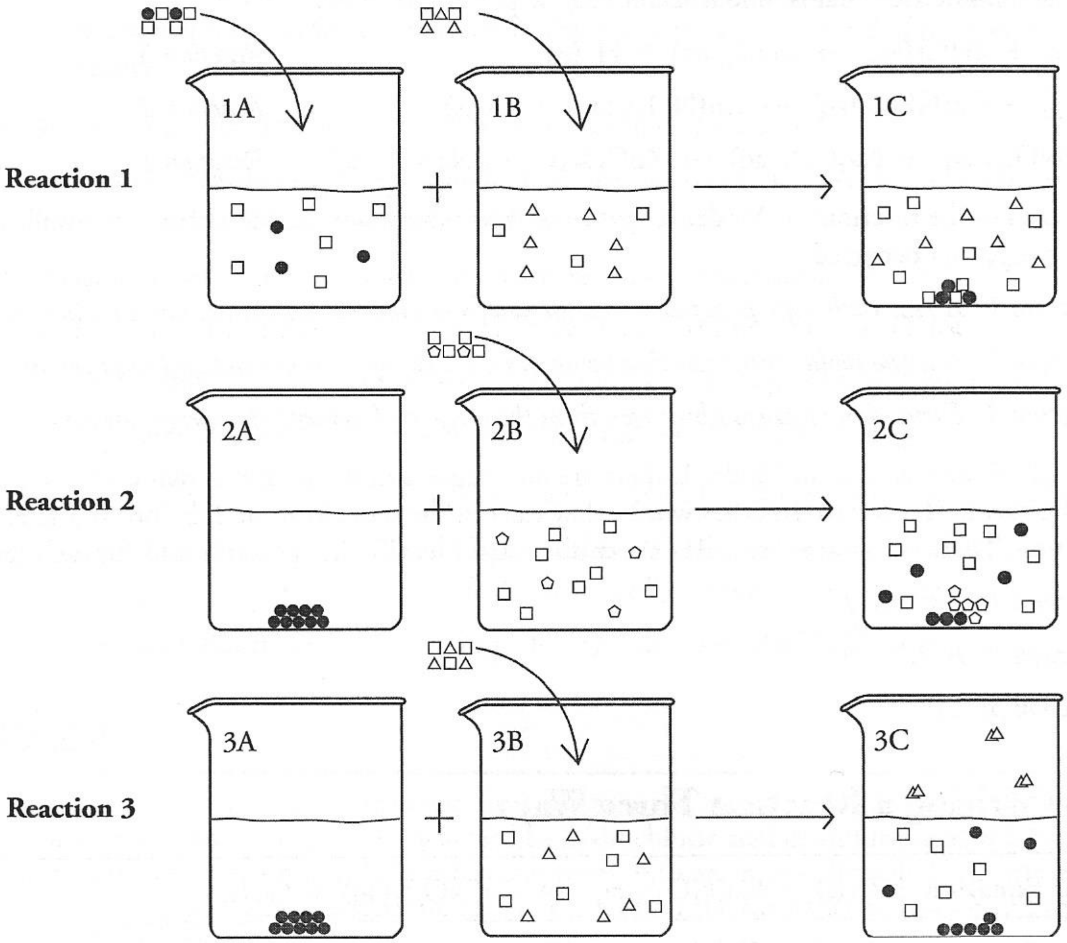
Net Ionic Equations

Do all reactant species participate in a reaction?

Why?

If you were to attend a sporting event on any random weekend you would find there are two types of people in attendance—players and spectators. Although both are important in their own right, they have different functions. This is also the case in chemical reactions. Although a species may be shown in a chemical reaction, it might only be a spectator. In other words it does not actually participate in the breaking and forming of chemical bonds that define the chemical reaction.

Model 1 – Three Reactions



1. Consider the three reactions in Model 1.
   a. Which beakers in the model contain solid, insoluble substances?
   1C, 2A, 2C, 3A, 3C
   b. What evidence is provided in the model to show that these substances are solids?
   The solids are shown as atoms touching. The circles are very close together in a regular pattern.

c. Which beakers in the model contain solutions of ionic substances?

1A, 1B, 1C, 2B, 2C, 3B, 3C

d. What evidence is provided in the model to show that these substances are ionic compounds?

Outside of the water they are solids, but when they go into the water, the ions divide as the substance dissolves.

2. Which of the reactions in Model 1 produces a gas?

Reaction 3 produces a gas.

3. Three reactions are provided below. Indicate which reaction in Model 1 corresponds to each reaction below. Discuss with your group members the evidence you used from Model 1 to match the reactions, and be prepared to support your choices to the class. Do not assume the reactions are stoichiometric. That is, one reactant may be present in excess.

$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$ *Reaction 3*

$Zn(s) + Cu(NO_3)_2(aq) \rightarrow Zn(NO_3)_2(aq) + Cu(s)$ *Reaction 2*

$Zn(NO_3)_2(aq) + Na_2CO_3(aq) \rightarrow ZnCO_3(s) + 2NaNO_3(aq)$ *Reaction 1*

4. For each of the reactions in Model 1, write a complete sentence that describes the specific chemical change that occurred.

Reaction 1: A zinc carbonate precipitate was formed from zinc and carbonate ions in solution.

Reaction 2: A single replacement reaction between zinc and copper ions produced solid copper.

Reaction 3: Formation of gaseous hydrogen from the single replacement of hydrogen by zinc.

5. In each of the reactions in Model 1, there are ions present in the solutions that do not participate in the chemical reaction. In other words, they exist in the same form both before and after the reaction. These substances are called **spectator ions**. Identify the spectator ions for each reaction.

Reaction 1: Na^{1+} NO_3^{1-}

Reaction 2: NO_3^{1-}

Reaction 3: Cl^{1-}

Model 2 – Writing a Reaction Three Ways

Molecular Equation	$Zn(s) + Cu(NO_3)_2(aq) \rightarrow Zn(NO_3)_2(aq) + Cu(s)$
Ionic Equation	$Zn(s) + Cu^{2+}(aq) + 2NO_3^{1-}(aq) \rightarrow Zn^{2+}(aq) + 2NO_3^{1-}(aq) + Cu(s)$
Net Ionic Equation	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

6. Consider the equations in Model 2.

a. Which equation represents the ionic substances as bonded together in the solution?

The molecular equation represents the ionic substances as bonded together in solution.

b. Which equation represents the ionic substances as separate ions in solution?

The ionic equation represents the ionic substances as separate ions in solution.

c. Which of the two equations from parts *a* and *b* is a better representation of how the species take part in the reaction?

The ionic equation is a better representation of what is actually happening in the reactions.

7. Compare the **net ionic equation** in Model 2 to the other two equations.

a. What chemical species is missing in the net ionic equation?

The nitrate ions are missing in the net ionic equation. These ions were spectator ions.

b. Explain why it is valid to remove this species from the equation.

The nitrate ion did not change during the reaction. It was the same charge and phase after the reaction as it was before the reaction. It does not take part in a chemical reaction, or a chemical change.

8. Work as a group to write a definition for a net ionic equation.

The net ionic equation is an equation that denotes the species that take an active part in a chemical reaction. The spectator ions are removed from the equation.

9. Write ionic and net ionic equations for the remaining reactions in Model 1.

a. Molecular Equation	$\mathrm{Zn\,(s) + 2HCl\,(aq) \rightarrow ZnCl_2\,(aq) + H_2\,(g)}$
Ionic Equation	$Zn\,(s) + 2H^{1+}\,(aq) + 2Cl^{1-}\,(aq) \rightarrow Zn^{2+}\,(aq) + 2Cl^{1-}\,(aq) + H_2(g)$
Net Ionic Equation	$Zn\,(s) + 2H^{1+}\,(aq) \rightarrow Zn^{2+}\,(aq) + H_2(g)$
b. Molecular Equation	$\mathrm{Zn(NO_3)_2\,(aq) + Na_2CO_3\,(aq) \rightarrow ZnCO_3\,(s) + 2NaNO_3\,(aq)}$
Ionic Equation	$Zn^{2+}\,(aq) + 2NO_3^{1-}\,(aq) + 2Na^{1+}\,(aq) + CO_3^{2-}\,(aq) \rightarrow ZnCO_3\,(s) + 2Na^{1+}\,(aq) + 2NO_3^{1-}\,(aq)$
Net Ionic Equation	$Zn^{2+}\,(aq) + CO_3^{2-}\,(aq) \rightarrow ZnCO_3\,(s)$

Read This!

When writing an ionic or net ionic equation for a reaction you must consider what species will divide into ions in solution. For example, strong acids like hydrochloric acid or sulfuric acid will be represented as ions, but weak acids remain mostly in molecular form so these are not divided. Similarly, only soluble ionic substances are represented as separate ions in solution. If the substance is insoluble, it remains written in the molecular form.

10. Write a molecular, ionic and net ionic equation for the reaction between acetic acid and sodium hydroxide.

Molecular Equation: $CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$

Ionic Equation: $CH_3COOH(aq) + Na^{1+}(aq) + OH^{1-}(aq) \rightarrow Na^{1+}(aq) + CH_3COO^{1-}(aq) + H_2O(l)$

Net Ionic Equation: $CH_3COOH(aq) + OH^{1-}(aq) \rightarrow CH_3COO^{1-}(aq) + H_2O(l)$

11. Write a molecular, ionic and net ionic equation for the reaction between solid magnesium carbonate and sulfuric acid.

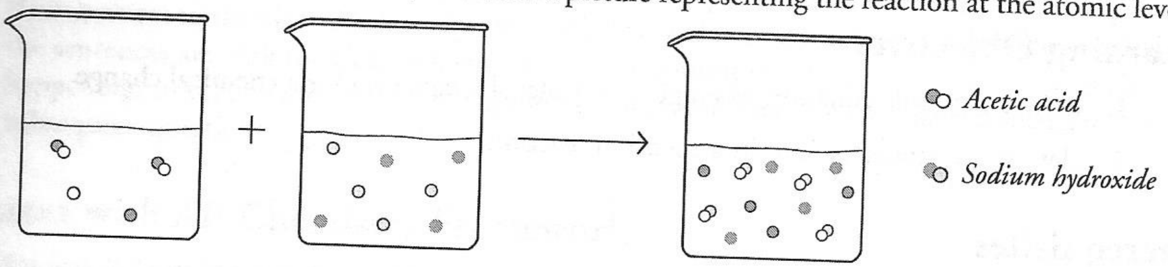
Molecular Equation: $MgCO_3(s) + H_2SO_4(aq) \rightarrow MgSO_4(s) + H_2O(l) + CO_2(g)$

Ionic Equation: $MgCO_3(s) + 2\,H^{1+}(aq) + SO_4^{2-}(aq) \rightarrow Mg^{2+}(aq) + SO_4^{2}(aq) + H_2O(l) + CO_2(g)$

Net Ionic Equation: $MgCO_3(s) + 2\,H^{1+}(aq) + SO_4^{2-}(aq) \rightarrow Mg^{2+}(aq) + H_2O(l) + CO_2(g)$

Extension Questions

12. Choose either Question 10 or 11, and draw a picture representing the reaction at the atomic level.



This drawing illustrates Question 10.

13. Is the law of conservation of mass obeyed in net ionic reactions? Support your answer with evidence from this activity.

Yes, the law of conservation of mass is obeyed in net ionic reactions. For example, in the equation

$$CH_3COOH(aq) + OH^{1-}(aq) \rightarrow CH_3COO^{1-}(aq) + H_2O$$

both sides of the reaction have two carbon atoms, four hydrogen atoms and three oxygen atoms.

14. In molecular equations, all substances are written as neutral, but in net ionic equations several of the species have charges. Is charge conserved in a net ionic equation? Support your answer with evidence from this activity.

Yes, charge is conserved in net ionic equations. For example in the equation

$$Zn(s) + 2H^{1+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

the total charge on the left side of the equation is 2+, and the total charge on the right side of the equation is 2+.

15. What are the advantages and disadvantages to using a net ionic equation to represent a chemical change rather than a molecular equation?

Advantages include representing only the species in the reaction that are part of the chemical change. This makes it easier to identify the bonds being broken and formed in the reaction. A net ionic equation is also shorter to write.

Disadvantages include not representing the ions that may be present in the beaker that may interfere with isolation of a product or use of a product in subsequent reactions.

Teacher Resources – Net Ionic Equations

Learning Objectives

1. Write a net ionic equation when given a molecular equation for a chemical change.
2. Identify the spectator ions in a chemical reaction.

Prerequisites

1. Students must know how to write and balance chemical reactions, including phase notations.
2. Students must understand what happens to ionic and molecular substances when they dissolve in water.
3. Students should understand the difference in ionization between a weak acid and a strong acid or a weak electrolyte and a strong electrolyte.
4. Students should have an understanding of the different types of reactions—acid/base, single replacement, double replacement, etc.

Assessment Questions

1. Identify the spectator ion(s) in the following chemical reaction:

   $KCl\,(aq) + AgNO_3\,(aq) \rightarrow KNO_3\,(aq) + AgCl\,(s)$

   a. K^{1+}

   b. Ag^{1+}

   c. K^{1+} and Ag^{1+}

   d. K^{1+} and $NO_3^{\ 1-}$

2. Write the ionic and net ionic equation for the following chemical reaction:

   $HNO_3\,(aq) + NaOH\,(aq) \rightarrow H_2O\,(l) + NaNO_3\,(aq)$

3. Write a molecular, ionic and net ionic equation for the reaction between concentrated nitric acid and solid zinc metal.

Assessment Target Responses

1. *d*

2. $H^{1+}(aq) + NO_3^{\ 1-}(aq) + Na^{1+}(aq) + OH^{1-}(aq) \rightarrow H_2O\,(l) + Na^{1+}(aq) + NO_3^{\ 1-}(aq)$

   $H^{1+}(aq) + OH^{1-}(aq) \rightarrow H_2O\,(l)$

3. $2HNO_3\,(aq) + Zn\,(s) \rightarrow H_2\,(g) + Zn(NO_3)_2\,(aq)$

   $2H^{1+}(aq) + 2NO_3^{\ 1-}(aq) + Zn\,(s) \rightarrow H_2\,(g) + Zn^{2+}(aq) + 2NO_3^{\ 1-}(aq)$

   $2H^{1+}(aq) + Zn\,(s) \rightarrow H_2\,(g) + Zn^{2+}(aq)$

Teacher Tip

- When all groups have finished with Question 4, ask a representative from each group to present their answers to the class. Most likely there will be a wide variety in how concise and detailed the sentences are. Ask the class to focus on the descriptions that best represent what is **really** happening. In other words, those that ignore the spectator ions. This will help students in the subsequent questions.

Alignment with AP Chemistry Framework

- **Essential Knowledge 3.A.1:** A chemical change may be represented by a molecular, ionic or net ionic equation.

  Learning Objective 3.2 The student can translate an observed chemical change into a balanced chemical equation and justify the choice of equation type (molecular, ionic or net ionic) in terms of utility for the given circumstance.

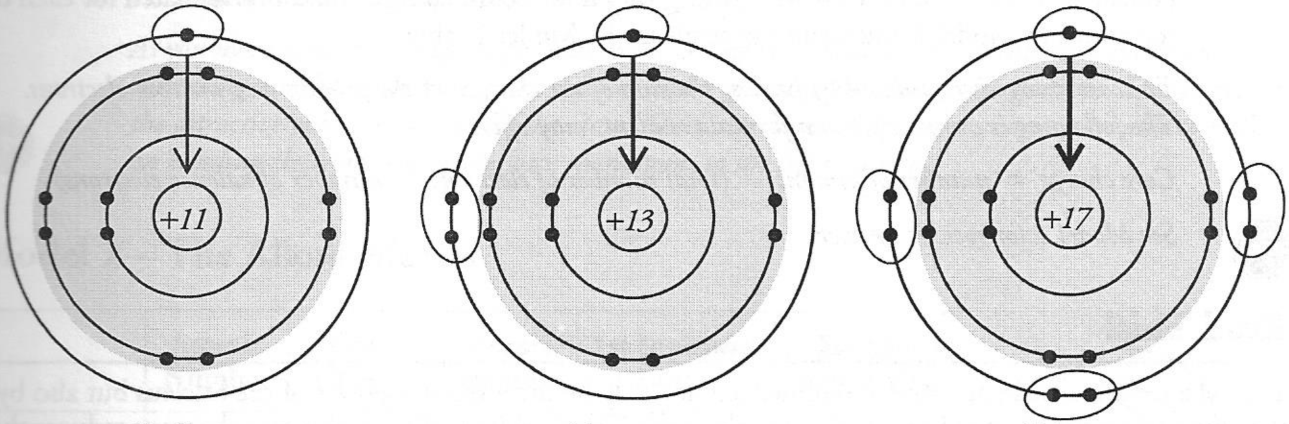
Advanced Periodic Trends

How do the particles in an atom interact to dictate periodic properties of elements?

Why?

Previously you have learned about Coulombic attraction and how it governs the trends in properties among the elements of the Periodic Table. For example, as you move across a period, atoms have more protons in the nucleus, which pulls the electrons in tighter making smaller, more electronegative atoms. As you proceed down a column of the periodic table, the valence electrons get further away, and the atoms get larger and less electronegative. Inquisitive students will always ask, "If more protons in the nucleus pull electrons in tighter, then why don't atoms get smaller when going down a column?" That is a good question, and one that you will investigate in this activity.

Model 1 – Period 3 Elements



Sodium Aluminum Chlorine

Atomic Number	*11*	*13*	*17*
Number of Electrons	*11*	*13*	*17*
Number of Valence Electrons	*1*	*3*	*7*
Core Charge	*+1*	*+3*	*+7*
Atomic Radius	186 pm	143 pm	99 pm
1st Ionization Energy	496 kJ/mol	578 kJ/mol	1251 kJ/mol
Electronegativity	0.9	1.5	3.0

1. Describe the relationship of the three elements in Model 1 with regard to their relative positions on the periodic table.

   The three elements are in the same row of the periodic table.

2. Refer to a periodic table to complete the first three rows of the table in Model 1.

   See Model 1.

3. Consider the charge and location of the protons in an atom.

   a. Indicate on the atomic drawings a total charge provided by the protons in the proper location for each atom.

   See Model 1.

   b. The number you just added to the diagrams in Model 1 is called the **nuclear charge**. Explain why this is an appropriate name for this value.

   The only charged particles in the nucleus are protons. Therefore, the total charge for the nucleus is equal to the charge on all the protons in the nucleus.

4. Circle the valence electron(s) in each of the atoms in Model 1.

   See Model 1.

5. In Model 1, the shaded circle in each atom indicates the core of the atom—the nucleus and the nonvalence electrons. Discuss with your group how a **core charge** could be calculated for each of the atoms in Model 1 and write the result in the Model 1 table.

   The core charge is calculated by finding the sum of the charges on the protons and the core electrons. The following is an example of a formula students may offer:

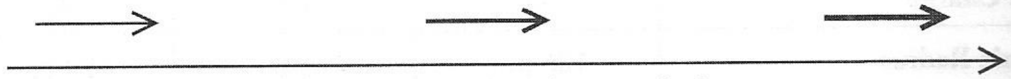
   Core charge = number of protons − (total number of electrons − number of valence electrons)

   See Model 1 for specific answers.

Read This!

The valence electrons in an atom are influenced not only by the attractive power of the nucleus but also by the repulsive power of neighboring and core electrons. The shielding effect of the core electrons reduces the attractive power of the nucleus. The pulling force that a valence electron actually feels, the **effective nuclear charge (Z^*)**, is much less than the nuclear charge because of this **shielding effect** of core electrons. Although the effective nuclear charge is difficult to calculate directly due to complex quantum effects within the atom, it is approximately equal to the core charge of an atom.

6. Use arrows like those below to illustrate the relative strength of the effective nuclear charge on the valence electrons in the atoms of Model 1.



Increasing effective nuclear charge = thicker arrow

   See Model 1.

7. According to Model 1, what happens to the effective nuclear charge of atoms as you move from left to right on the periodic table?

   As you move from left to right across a row of the periodic table, the effective nuclear charge increases.

8. Explain the trend as you move across a row of the periodic table for each of the following atomic properties using your understanding of effective nuclear charge.

   a. Atomic radius

   Atoms in a row have the same number of electron shells. As you move from left to right, the number of protons increases. Because the number of core electrons remains constant, the effective nuclear charge increases and the valence electrons experience a stronger nuclear pull and the atomic radius decreases.

   b. Ionization energy

   As you move across a row of the periodic table, the effective nuclear charge increases due to a larger number of protons in the nucleus but a constant number of core electrons. This increases the pull on the valence electrons by the core of the atom making it more difficult to remove an electron. Thus, the ionization energy increases.

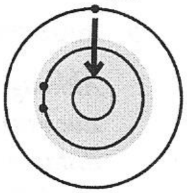
   c. Electronegativity

   As you move across a row of the periodic table, the effective nuclear charge increases due to an increasing number of protons in the nucleus and a constant number of core electrons. This increases the attractive power of the core of the atom. Thus, the atoms to the right in a row are able to pull on bonding electrons with more force than atoms to the left in a row.

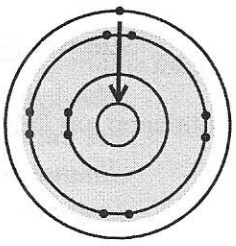
Model 2 – The Alkali Metals

	Atomic Number	Core Charge	Atomic Radius	1st Ionization Energy	Electro-negativity
Lithium	*3*	*+1*	152 pm	520 kJ/mole	0.91
Sodium	*11*	*+1*	186 pm	496 kJ/mole	0.87
Potassium	*19*	*+1*	227 pm	419 kJ/mole	0.73

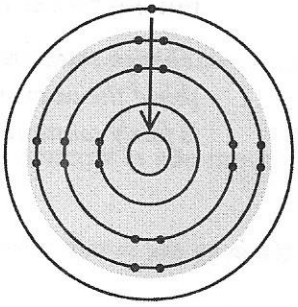
Lithium



Sodium



Potassium



9. Describe the relationship of the three elements in Model 2 with regards to their relative positions on the periodic table.

   The three elements of Model 2 are found in the same column of the periodic table, and appear in the order shown.

10. Draw a circle and lightly shade the area representing the core of each atom in Model 2.

    See Model 2.

11. Refer to a periodic table to complete the table in Model 2.

    See Model 2.

12. According to Model 2, what happens to the effective nuclear charge of atoms as you move from the top to the bottom of a column on the periodic table?

The effective nuclear charges for all atoms in a column of the periodic table are identical.

13. Is effective nuclear charge a factor in how periodic properties change within a column of the periodic table? If no, propose another factor that would influence the attractive forces between the nucleus and valence electrons in an atom.

No, since the effective nuclear charge for all elements in a column is the same, it cannot explain the gradual change in properties observed as you move down a column. Instead, the distance between the valence electrons and the nucleus causes property changes.

14. Use arrows like those in Model 1 to illustrate the relative strength of attraction between the nucleus and the valence electrons in the atoms of Model 2.

See Model 2.

15. Explain the trend as you move down a column of the periodic table for each of the following atomic properties using your understanding of effective nuclear charge and any other factors that might govern periodic trends.

a. Atomic radius

Although the number of protons increases as you go down a column of the periodic table, the effective nuclear charge does not because the number of core electrons also increases. Therefore, it is the distance between the valence electrons and the nucleus that governs the trend. Atoms with more electrons are larger because electrons are located farther from the nucleus as the number of shells increases.

b. Ionization energy

Although the number of protons increases as you go down a column of the periodic table, the effective nuclear charge does not because the number of core electrons also increases. Therefore, it is the distance between the valence electrons and the nucleus that governs the trend. As the valence electron gets farther from the nucleus, the attractive power of the nucleus decreases and it takes less energy to remove an electron.

c. Electronegativity

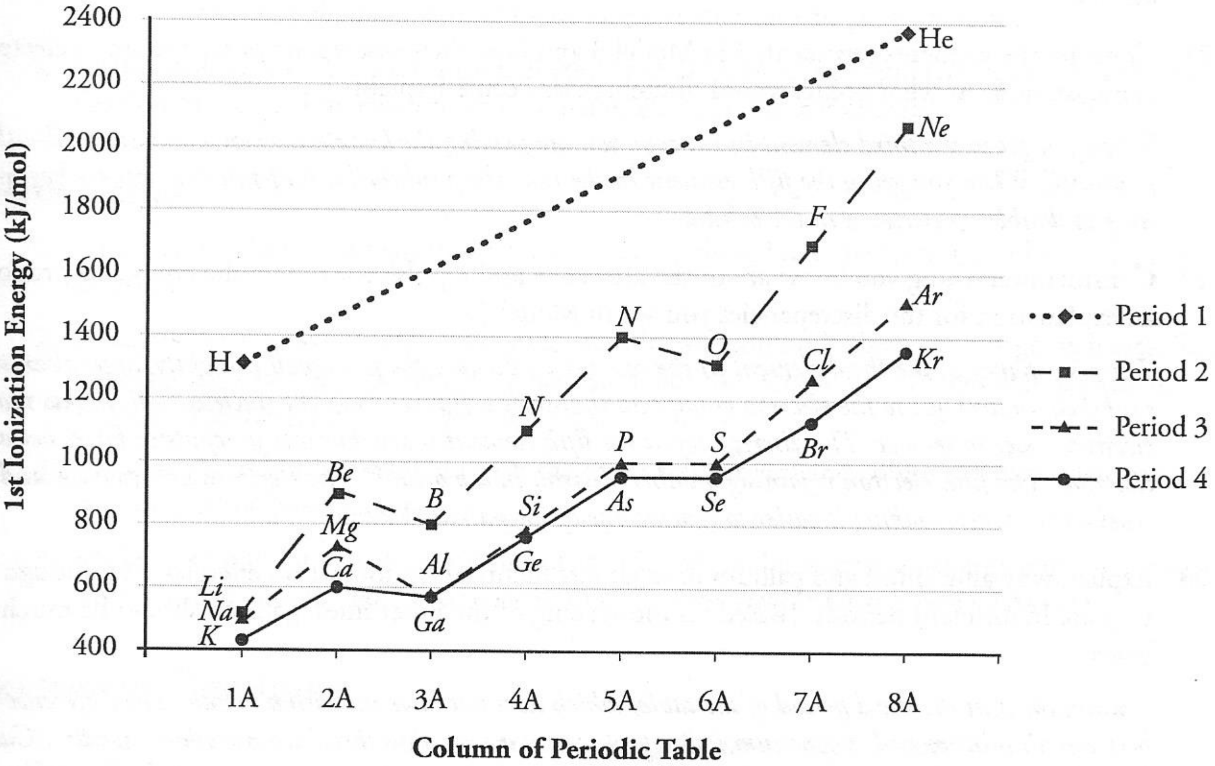
Although the number of protons increases as you go down a column of the periodic table, the effective nuclear charge does not because the number of core electrons also increases. Therefore, it is the distance between the valence electrons and the nucleus that governs the trend. As the atom gets larger, the nuclear pull exerted on bonding electrons decreases.

16. Answer the question posed in the *Why?* box at the start of this activity: "If more protons in the nucleus pull electrons in tighter, then why don't atoms get smaller when going down a column?"

Though there are more protons as you move down a column, there are also more core electrons that shield the valence electrons from feeling the pull of those protons. Therefore, the effective nuclear charge is fairly constant within a column.

Extension Questions

Model 3 – Ionization Energies



17. Refer to the graph in Model 3.

   a. What property of atoms does the graph illustrate?

   The graph illustrates the ionization energies of atoms of different elements.

   b. There are four lines on the graph. What do the lines represent?

   The four lines on the graph represent the elements in the first four periods of the periodic table.

   c. Two elements, hydrogen and helium, have been labeled on the graph. Label the remaining elements on the graph. You should finish with krypton.

   See Model 3.

18. How does the graph in Model 3 illustrate the periodic trend for ionization energy as you move across a row of the periodic table?

   Each line on the graph represents a period. The lines, in general, have positive slopes showing the trend that ionization energy increases as you move across the table.

19. How does the graph in Model 3 illustrate the periodic trend for ionization energy as you move down a column of the periodic table?

   Each of the four lines starts and remains lower than the ones above it. This shows that as you go down the periodic table, ionization energies decrease.

20. Are either of the trends you described in Questions 18 and 19 perfect? If not, where are the "blips" or discrepancies in the trends? Do they always occur in the same place?

    There are regular discrepancies in the trends for the third element in the row and the fifth element in the row.

21. Consider the elements represented in Model 3 and how their discrepancies may relate to electron configuration. At what points would discrepancies occur? Explain.

    When you get to the third element in the row, you are placing the last electron in a new subshell—the p subshell. When you get to the fifth element in the row, the p subshell is half-full and you are beginning to double up electrons in the orbitals.

22. Consider everything you know about the attractive and repulsive forces in the atom and propose an explanation for the discrepancies you see in Model 3.

    The discrepancy at the third element in the row occurs because the p subshell is slightly larger than the s subshell on average, so the electron going into that shell is further from the nucleus. This makes that electron easier to remove. The discrepancy at the fifth element is attributable to repulsive forces between electrons. The fifth electron is joining another electron in a p orbital. The electrons are crowded and repel one another, making it easier to remove one of the paired electrons.

23. Explain why aluminum and gallium have almost identical 1st ionization energies even though they are in different periods. (Based on the spacing of the other lines, gallium should be much lower.)

    Aluminum is in the third period of the table, which does not have transition metals. The difference between aluminum and magnesium is one proton and a new p subshell in the atomic structure. Gallium, however, is in the fourth period of the table, which does include transition metals. The difference between calcium and gallium is 11 protons, a filled d subshell and a new p subshell. All of those additional protons in the nucleus make it more difficult to remove the electron in the p subshell, so gallium's ionization energy is much higher than would be predicted by the previous periods.

Teacher Resources – Advanced Periodic Trends

Learning Objectives

1. Calculate the core charge to approximate effective nuclear charge in an atom.
2. Justify atomic radius, 1st ionization energy or electronegativity trend data using the concepts of Coulombic attraction, electron shielding and effective nuclear charge.

Prerequisites

1. Students should understand the attractive and repulsive forces between the subatomic particles in an atom.
2. Students should have a qualitative understanding of Coulomb's law—as charge increases, force increases; as distance increases, force decreases. See the "Coulombic Attraction" activity in *POGIL Activities for High School Chemistry.*
3. Students should be comfortable with the terms row, period and column as they relate to the structure of the periodic table.
4. Students should know the definitions of atomic radius, 1st ionization energy and electronegativity. See the "Periodic Trends" activity in *POGIL Activities for High School Chemistry.*

Assessment Questions

1. What is the approximate effective nuclear charge for an atom of Silicon?

   a. +14

   b. +10

   c. +4

   d. 0

2. Which of the following properly explains why an atom of aluminum has a lower electronegativity than an atom of sulfur?

   a. Aluminum is a larger atom.

   b. Aluminum has fewer filled atomic orbitals.

   c. Sulfur has a larger effective nuclear charge.

   d. Sulfur has more electrons.

3. Electron affinity is the energy released when a gaseous atom captures a free electron and becomes a +1 anion. Use the concepts of Coulombic attraction and repulsion, shielding, and effective nuclear charge to predict the trend in electron affinity as you move across a row of the periodic table.

Assessment Target Responses

1. *c*
2. *c*
3. *As you move across a row of the periodic table, the effective nuclear charge of an atom increases. This gives the atom a stronger attraction to the free electron. The electron will fill an orbital in the same energy level for all atoms in the row so distance from the nucleus is not a significant factor. Therefore more energy will be released from atoms on the right of the table than those on the left. Electron affinity is expected to increase as you move across a row of the periodic table. Of course, there will be exceptions to this trend just as there are for ionization energy.*

Teacher Tip

- Students should be encouraged to discuss periodic trends from an energy perspective rather than one of "happy atoms." Explaining that a half-full or full orbital or sublevel makes an atom more stable is not a strong argument for the trends. Rather, ask students to consider what factors make the attraction to the electron stronger or weaker within the atom.

Alignment with AP Chemistry Framework

- **Essential Knowledge 1.C.1:** Many properties of atoms exhibit periodic trends that are reflective of the periodicity of electronic structure.

  Learning Objective 1.9 The student is able to predict and/or justify trends in atomic properties based on location on the periodic table and/or the shell model.

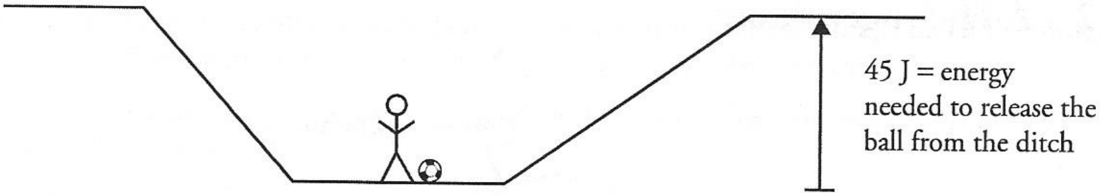
Photoelectron Spectroscopy

What does a photoelectron spectrum tell us about the structure of an atom?

Why?

When scientists first discovered X-rays, they realized they could do more than just make images of people's bones. X-rays could also allow them to "see" inside the atom. They could not do this directly, but in looking for patterns in ionization energy data they were able to determine the energy levels and sublevels of electrons and how many electrons were in each level.

Model 1 – A Soccer Player in a Ditch



1. Consider Model 1. Imagine that a soccer player is trying to kick a ball out of a ditch.
   a. What force of attraction is keeping the soccer ball at the bottom of the ditch?

   Gravity is keeping the soccer ball in the ditch.

   b. Which type of energy must be overcome to get the ball out of the ditch—potential or kinetic?

   Gravity is potential energy.

   c. Which type of energy must the ball have to get out of the ditch—potential or kinetic?

   The ball must have kinetic energy to get out of the ditch.

2. How much energy must be given to the ball by kicking it to get it out of the ditch?

   The ball needs at least 45 J of energy to leave the ditch.

3. Describe what happens to the ball if the soccer player's kick provides:
   a. 30 J of energy to the soccer ball in the ditch.

   The ball would not reach the top of the ditch and would roll back down to the bottom.

   b. 45 J of energy to the soccer ball in the ditch.

   The ball will get to the top of the ditch and stop.

   c. 60 J of energy to the soccer ball in the ditch.

   The ball will leave the ditch and keep moving.

4. For each of the scenarios in Question 3 where the ball successfully leaves the ditch, determine the kinetic energy the ball will have when it reaches the top of the ditch.

   a. *The ball does not leave the ditch.*

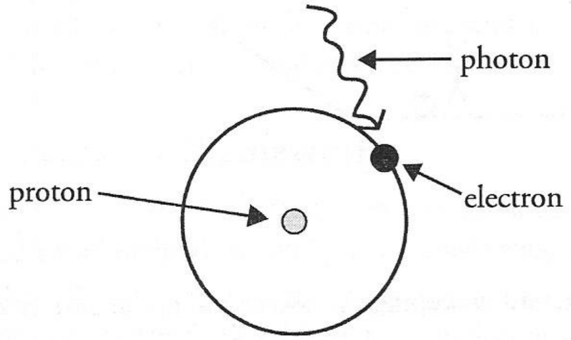
   c. *The ball leaves the ditch and has zero KE at the top.*

   d. *The ball leaves the ditch and has 15 J of KE at the top.*

5. Construct an algebraic equation that shows the relationship among the energy of the player's kick (KE_{kick}), the potential energy of gravity on the ball (PE) and the kinetic energy the ball will have as it leaves the ditch (KE_{roll}).

$KE_{kick} = PE + KE_{roll}$

Model 2 – A Hydrogen Atom



6. Refer to Model 2.

   a. What force of attraction holds the electron in the hydrogen atom?

   There is Coulombic attraction between the positively-charged nucleus and the electron.

   b. Which type of energy needs to be overcome to remove an electron from the atom—potential or kinetic?

   Coulombic attraction is potential energy.

   c. What is supplying the energy to remove the electron from the atom in Model 2?

   The photon is supplying the energy to remove the electron.

7. Fill in the table below to show how the hydrogen atom (Model 2) parallels the ball in the ditch analogy (Model 1).

Soccer Ball in the Ditch	**Hydrogen Atom**
Gravity	*Coulombic Attraction*
Ball	*Electron*
Player's kick	*Photon*

8. Consider the atom in Model 2.

   a. If the photon has less than the minimum energy needed to eject the electron from the atom, what will happen to the electron?

   The electron will stay in the atom.

   b. If the photon has exactly the minimum energy needed to eject the electron from the atom, what will happen to the electron?

   The electron will be removed from the atom, but will have zero KE after being removed.

   c. If the photon has more than the minimum energy needed to eject the electron from the atom, what will happen to the electron?

   The electron will be removed from the atom and will have some KE after being removed.

9. The amount of energy necessary to remove an electron from an atom is called the **ionization energy**. What part of the analogy in Model 1 represents the ionization energy?

   The ionization energy in Model 2 is analogous to the 45 J of energy needed to get the ball out of the ditch in Model 1.

10. What is the relationship between the ionization energy of an electron and the net attractive force that holds an electron in an atom?

    The ionization energy is equal to, but opposite in sign to the Coulombic attraction that holds an electron in an atom.

11. The electrons that escape the atom after bombardment by a photon are called **photoelectrons**. Why might this be an appropriate name for these electrons?

    Photoelectrons is an appropriate name because they are electrons that have been removed from an atom by high energy photons.

Read This!

Photoelectron spectroscopy (PES) allows scientists to determine the ionization energy of not only valence electrons, but all electrons in an atom. In PES, a gaseous sample of atoms is bombarded by X-rays or ultraviolet light (photons) of known energy. The kinetic energies of the photoelectrons that are ejected from the atoms are measured. The number of photoelectrons with the same kinetic energies is noted. Although only one electron is removed from each atom, several atoms are ionized in the experiment. The electron that is removed will differ from atom to atom. The collective result provides information about all the electrons in an atom of the sample.

12. Construct an algebraic equation that shows the relationship between the energy of the photon (KE_{photon}), the ionization energy (IE) and the kinetic energy of the photoelectron ($KE_{electron}$) as it leaves the atom.

    $KE_{photon} = IE + KE_{electron}$

13. If the kinetic energy of the photon is exactly equal to the ionization energy, the kinetic energy of the photoelectron should be zero. Verify that your equation is consistent with this idea. If not, revise your equation.

Example: $KE_{photon} = 30\ kJ/mole;\ IE = 30\ kJ/mole$

$30\ kJ/mole = 30\ kJ/mole + 0\ kJ/mole$

14. Consider the equation you wrote in Question 12. What pieces of data do you need to know to calculate the ionization energy of a given electron?

To calculate the ionization energy of a given electron, you need to know the energy of the photons used in the experiment and the kinetic energy of the electrons after they are removed from the atom.

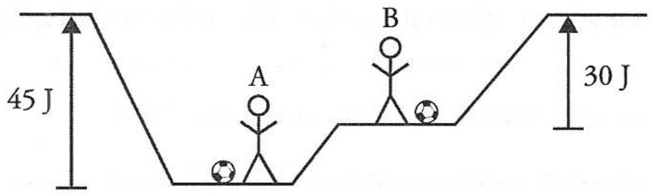
15. A photoelectron experiment is performed on a sample of silicon using photons with an energy of 1.43×10^5 kJ/mole. Photoelectrons are generated that have a kinetic energy of 1.34×10^5 kJ/mole. What was the ionization energy of these electrons?

$IE = 1.43 \times 10^5\ kJ/mole - 1.34 \times 10^5\ kJ/mole = 9 \times 10^3\ kJ/mole$

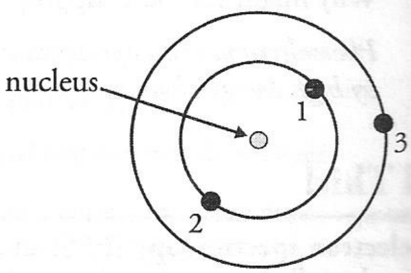
16. In the previous question, was only one atom of silicon involved, or were many atoms involved? What evidence do you have from the question to support your answer?

Theoretically, a mole of electrons was removed because the units on the energies are "per mole."

Model 3 – Multiple Energy Levels



Soccer Balls in a Ditch



Lithium Atom

17. In the ditch diagram in Model 3, which player (A or B) will need to put more energy into their soccer ball to get it out of the ditch? Explain your answer in terms of both depth and potential energy.

Player A will need to kick the ball harder (put in more energy) to get it out of the ditch. Player A's ball is deeper in the ditch and therefore has a greater attraction to the Earth, meaning it is attracted with more potential energy.

18. Consider the electrons in an atom of lithium as diagrammed in Model 3. Which electron, 1 or 3, will require more energy to be removed? Support your answer by discussing the attractive forces in the atom and how they might be different for electrons 1 and 3.

Electron 1 will need more energy to be removed from the atom because it is closer to the nucleus, meaning it has a greater attraction.

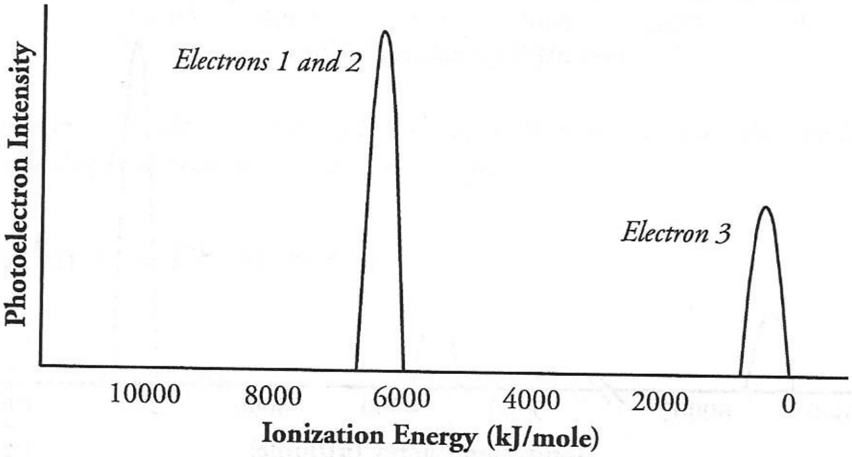
19. Compare electrons 1, 2 and 3 in terms of their ionization energy. Explain your reasoning.

    Electrons 1 and 2 have the same ionization energy because they are equidistant from the nucleus. Electron 3 has an ionization energy lower than electrons 1 or 2 because it is farther from the nucleus.

20. If a large number of lithium atoms are ionized in a PES experiment, each losing one randomly chosen electron, which ionization energy will be recorded more often, the lower IE or the higher IE? Justify your answer.

    The higher ionization energy (for electrons 1 and 2) would be recorded more often because there is a greater probability that one of those electrons is ejected compared to the one electron (electron 3) that has the lower ionization energy.

Model 4 – Photoelectron Spectra of Lithium



21. Refer to the graph in Model 4.

    a. What are the units of the *x*-axis?

    kJ/mole

    b. What is unusual about the way the *x*-axis values are graphed?

    The lower IE values are on the right, the higher values are on the left.

    c. Which of the peaks in the graph represents electrons that are more tightly held by the nucleus? Explain your reasoning.

    The peak on the left represents electrons with larger ionization energy values, so they are held more tightly by the nucleus of the atom.

22. How many atoms of lithium were ionized (theoretically) in order to obtain the data for the spectrum above?

    A mole of lithium atoms was ionized (theoretically) to get these data.

23. Based on the energy values of the peaks, label each peak with the electrons in a lithium atom (see Model 3) to which they correspond.

    See Model 4.

24. Why are there only two peaks and not three in the lithium spectrum in Model 4?

    Two of the electrons in lithium have the same ionization energy, so there are only two peaks.

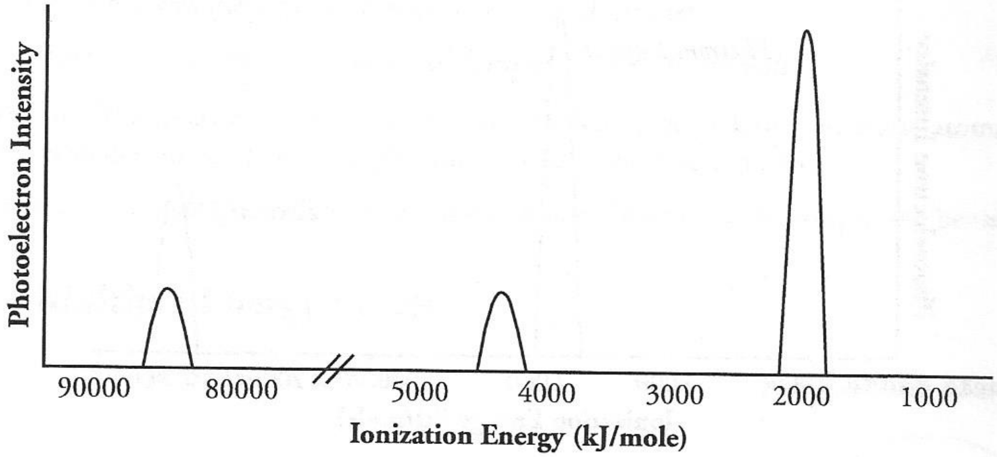
25. Why is the higher energy peak about twice as high as the lower energy peak?

    The higher energy peak represents two electrons (1 and 2), while the lower energy peak represents only one electron (3). The higher energy peak has a higher photoelectron intensity because it represents ejection and detection of two electrons.

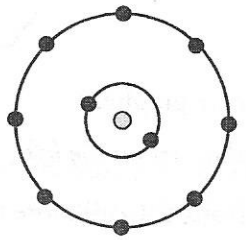
26. What does the number of peaks in a PES spectrum reveal about the energy sublevels occupied by electrons in an atom?

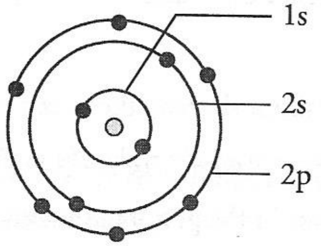
    The number of peaks in a spectrum is equal to the number of sublevels for electrons in the atom.

27. If the photoelectric spectrum of Ne is:



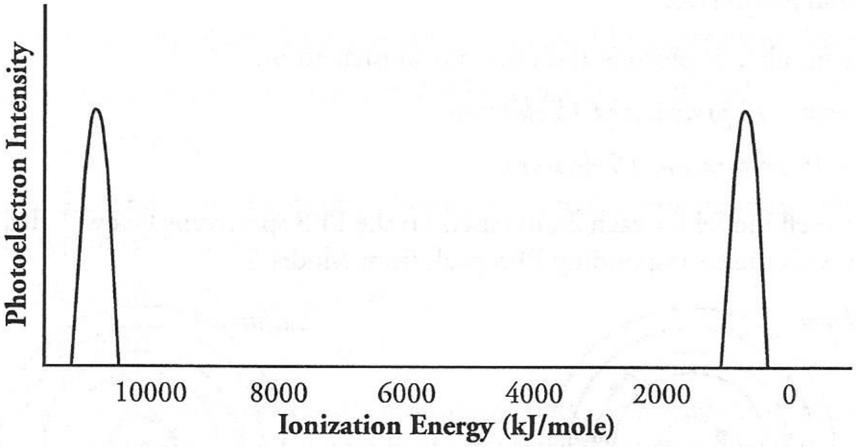
Which shell model below best matches this spectrum? Explain your reasoning in one or two complete sentences.





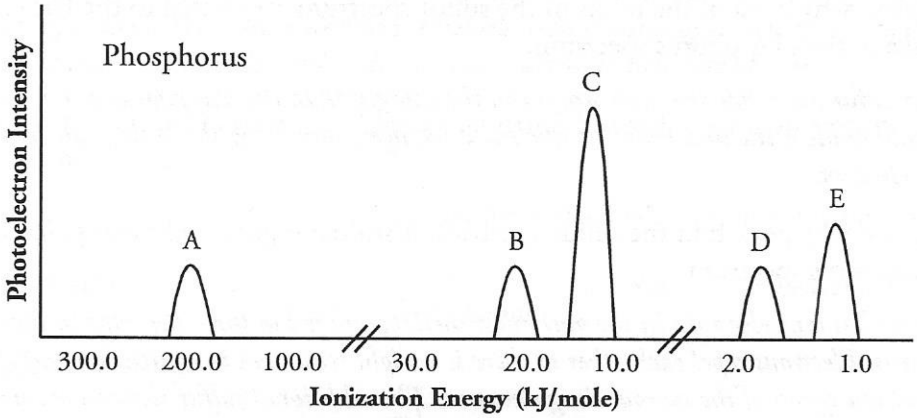
The shell model on the right best matches the spectrum above because the spectrum has three peaks and the shell model on the right has three energy sublevels. Moreover, the low energy peak has a higher intensity attributable to the larger number of valence electrons compared to core electrons.

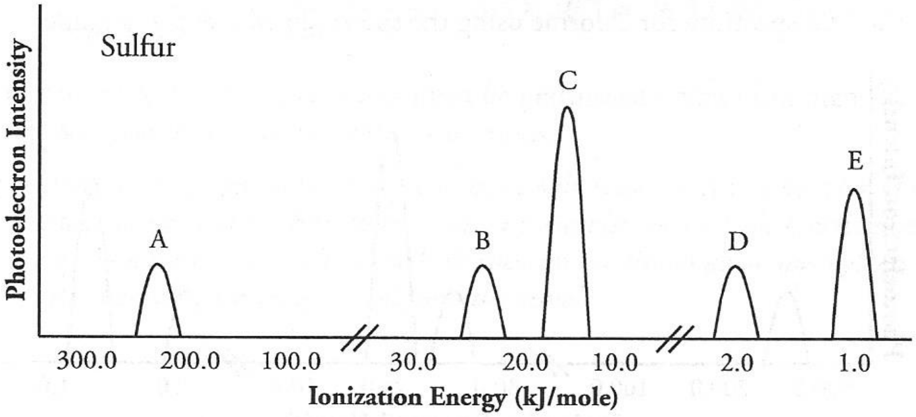
28. Look back at Model 4. Using the lithium PES spectrum as a starting point, show how the spectrum of the next larger element (beryllium) might be different. (Recall that Be will have one more proton in its nucleus and one more electron in its sublevels.)



Exact placement of peaks is not expected here, but students should know that the IE for both peaks will increase and that both peaks will be the same height.

Model 5 – Sulfur and Phosphorus





29. Refer to Model 5.

   a. The atomic structure of which atoms are represented by the PES spectra shown?

   Sulfur and phosphorus.

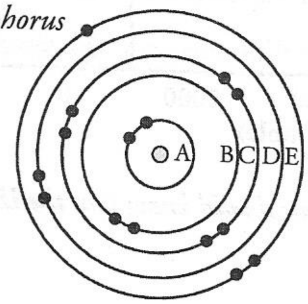
   b. List the number of protons and electrons in each atom.

   Phosphorus—15 protons and 15 electrons.

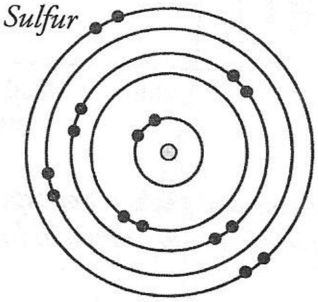
   Sulfur—16 protons and 16 electrons.

   c. Draw a shell model for each atom based on the PES spectrums below. Label each shell in your models with the corresponding PES peak from Model 5.

Phosphorus



Sulfur



30. Consider the attractive and repulsive forces in the atoms of sulfur and phosphorus.

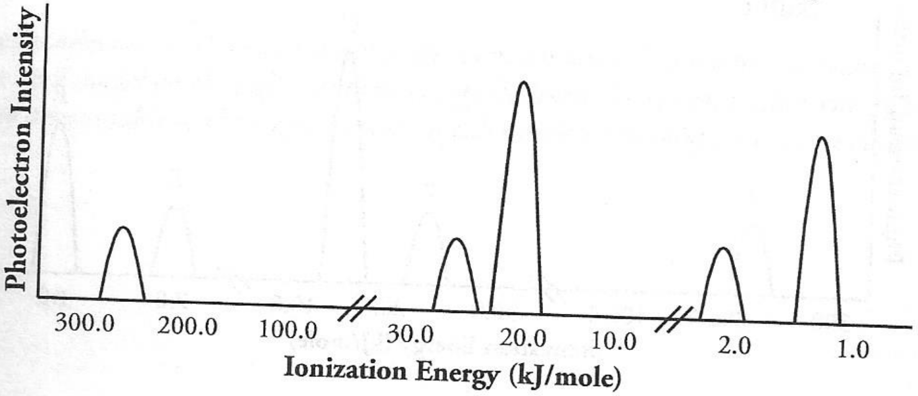
   a. Explain why most of the peaks in the sulfur spectrum are shifted to the left relative to the peaks in the phosphorus spectrum.

   The sulfur atom has one more proton in the nucleus than the phosphorus atom. Therefore the pull of coulombic attraction from the nucleus is stronger, increasing the ionization energy of (almost) all the electrons.

   b. Explain why peak E in the sulfur spectrum is shifted slightly right compared to peak E in the phosphorus spectrum.

   Sulfur has four electrons in the outermost shell, compared to three electrons in that shell for phosphorus. Electrons repel each other so there is a slight reduction in ionization energy because of the repulsion effects of the surrounding electrons. The additional sulfur electron occupies a half-filled 3p orbital, thus causing electron–electron repulsion.

31. Sketch the PES spectrum for chlorine using the spectra in Model 5 as a guide.



Extension Questions

32. PES experiments frequently use an X-ray wavelength of 0.8340 nm. Recall that the energy of a photon can be calculated using the equation $E = hc/\lambda$.

    a. Calculate the energy of the X-ray photon used in the PES experiment described.

    $$KE_{photon} = (6.626\times 10^{-34}\ J/s)(3.000\times 10^{8}\ m/s)/(0.8340\times 10^{-9}\ m)$$
    $$= 2.383\times 10^{-16}\ J$$

    b. Calculate the ionization energy of a photoelectron with a kinetic energy of 2.372×10^{-16} J. Include appropriate units.

    $$IE = 2.383\times 10^{-16}\ J - 2.372\times 10^{-16}\ J$$
    $$= 0.011\times 10^{-16}\ J = 1.1\times 10^{-18}\ J$$

    c. The value you have calculated is the ionization energy of a single electron. Generally we express the ionization energy of a mole of electrons. What would be the ionization energy of a mole of the electrons from part *a*? Include appropriate units and significant figures.

    $$(1.1\times 10^{-18}\ J/electron)(6.02\times 10^{23}\ electrons/mole) = 6.6\times 10^{5}\ J/mole = 660\ kJ/mole$$

33. How are photoelectron spectroscopy and the photoelectric effect related?

    The photoelectric effect discovered by Heinrich Rudolf Hertz and later explained by Einstein, is the phenomenon observed when incident electromagnetic waves with sufficient energy ionize the atoms on the surface of a metal and release electrons. Photoelectron spectroscopy is an application of the photoelectric effect that is used to determine the internal electronic structure of atoms.

34. What is the maximum wavelength of light that could be used to eject an electron with an ionization energy of 340 kJ/mole?

    The photon's energy would need to at least equal the ionization energy of a single electron.

    $$IE_{electron} = 3.40\times 10^{5}\ J/mole\left(\frac{1\ mole}{6.022\times 10^{23}\ electrons}\right) = 5.65\times 10^{-18}\ J/electron$$

    $$E = hc/\lambda \ \ or \ \ \lambda = hc/E$$

    $$\lambda = \frac{(6.626\times 10^{-34}\ J\cdot s)\left(3.00\times 10^{8}\ \frac{m}{s}\right)}{5.65\times 10^{-18}\ J/electron} = 3.5\times 10^{-8}\ m = 35\ nm$$

35. Photoelectron spectroscopy experiments must be performed under ultra-high vacuum conditions. Propose a reason for these extreme conditions.

    The high energy electrons that are ejected from the sample must travel to a detector. If air was present, the electrons would surely bump into other atoms or molecules, gain or lose kinetic energy and/or be deflected away from the detector. The ultra-high vacuum conditions allow the high energy electrons a free path to the detector after being ejected from the sample.

Teacher Resources – Photoelectron Spectroscopy

Learning Objectives

1. Derive the mathematical relationship between kinetic energy, ionization energy and photon energy in a PES experiment using a conservation of energy argument.
2. Match proposed shell models of atoms with photoelectron spectrums of those atoms.
3. Compare PES spectra of atoms with similar atomic numbers, and explain why peaks might be shifted to the left or right because of changes in the structure of the atoms.

Prerequisites

1. Students should be able to qualitatively determine relative potential energies of electrons inside an atom based on a shell model (Coulomb's law).
2. Students should have working definitions of potential (attractive) and kinetic (in motion) energy.
3. Students should be able to draw electrons in energy shells to represent the fact that electrons exist in discrete energy levels.
4. Students should be able to describe light in both the wave and particle (photon) pictures.

Assessment Questions

1. A photoelectron experiment is performed on a sample of calcium using photons having energy of 123 MJ/mole. The ionization energy of an electron in the 2nd energy level of calcium is 34 MJ/mole. What is the kinetic energy (in MJ/mole) of the photoelectrons that are generated?

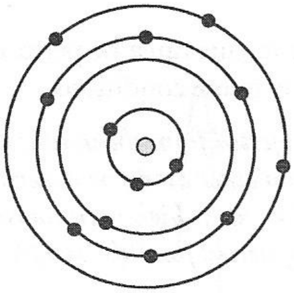
   a. 89 MJ/mole

   b. 157 MJ/mole

   c. −89 MJ/mole

   d. 6.24 MJ/mole

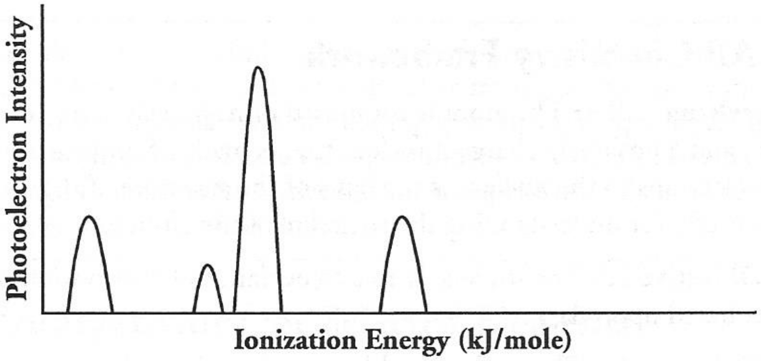
2. Researchers from the planet Zorba have discovered an atom with the following electron structure (shown as a shell model). Sketch the photoelectron spectrum that the researchers analyzed to obtain this knowledge of atomic structure.



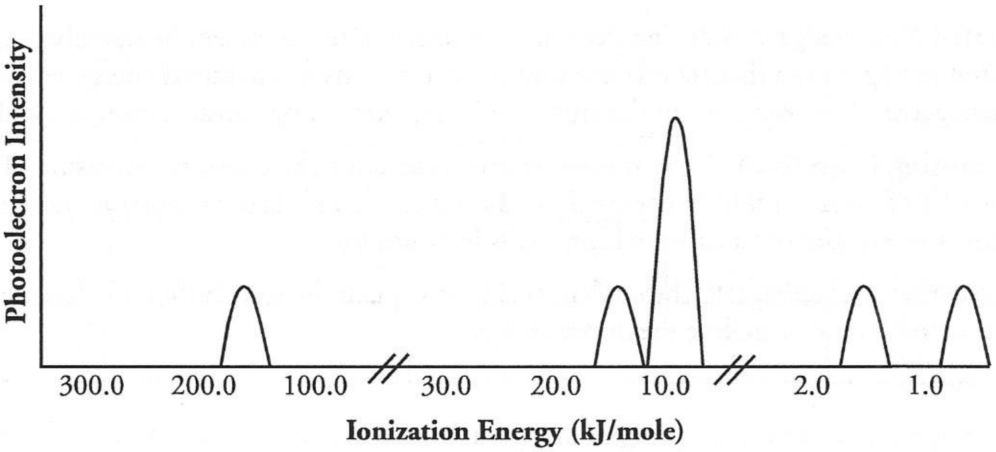
3. Sketch a PES spectrum of silicon using the spectra in the activity as a guide.

Assessment Questions Target Responses

1. *a*
2.



3.



Teaching Tips

- It would be useful to begin the class with a short review or activity that draws to mind Coulomb's law and the attraction of electrons to the nucleus of an atom.
- Some students will confuse PES with the more familiar hydrogen emission spectra they learned when studying the Bohr atomic model. Be sure to point out that in the Bohr model, electrons do not escape from the atom. The photons in the visible range have only enough energy to move electrons from one energy level to another. In photoelectron spectroscopy however, the electrons absorb so much energy from the X-rays or ultraviolet rays that they are ejected completely from the atom.
- In this activity, we have chosen to give simulated photoelectron spectra. The reasons for this are mainly that actual spectra have a great deal of background noise and because not all theoretical peaks can be detected on a single spectrograph. The lowest ionization energy of lithium shown above is not listed as a photoelectron peak in the source used (http://xdb.lbl.gov/Section1/Table_1-1.pdf), but is in fact the first ionization energy of lithium. In other words, simplicity over actual data has been chosen because real data might lead to greater confusion than it is worth. All values are, however, correct.

- There are several ways to display a PES spectrum. Some use an *x*-axis with increasing values. Some break up the spectrum into several pieces. It would be a good idea to expose students to several different displays after they have completed this activity. A good website to use for this purpose is http://www.chem.arizona.edu/chemt/Flash/photoelectron.html.

Alignment with AP Chemistry Framework

- **Essential Knowledge 1.B.1:** The atom is composed of negatively charged electrons, which can leave the atom, and a positively charged nucleus that is made of protons and neutrons. The attraction of the electrons to the nucleus is the basis of the structure of the atom. Coulomb's Law is qualitatively useful for understanding the structure of the atom.

  Learning Objective 1.5 The student is able to explain the distribution of electrons in an atom or ion based upon data.

  Learning Objective 1.6 The student is able to analyze data relating to electron energies for patterns and relationships.

- **Essential Knowledge 1.B.2:** The electronic structure of the atom can be described using an electron configuration that reflects the concept of electrons in quantized energy levels or shells; the energetics of the electrons in the atom can be understood by consideration of Coulomb's Law.

  Learning Objective 1.7 The student is able to describe the electronic structure of the atom, using PES data, ionization energy data, and/or Coulomb's Law to construct explanations of how the energies of electrons within shells in atoms vary.

  Learning Objective 1.8 The student is able to explain the distribution of electrons using Coulomb's Law to analyze measured energies.

Types of Bonds

How can one determine if a bond between two atoms is ionic, covalent or metallic?

Why?

Chemical bonding is all about having a full valence shell of electrons. However, there are various ways to accomplish this goal. Atoms can share electrons with other atoms, or steal electrons from other atoms. Linus Pauling used scientific data to devise a numbering system, which quantifies an atom's ability to attract an electron from another atom. These values are shown in Model 1. You can think of these electronegativities as the ranking of members in a prizefighting competition. All contestants are fighting to get the ultimate prize—an electron to fill their shell.

Model 1 – Electronegativities for Selected Elements

IA	*IIA*	*IIIA*	*IVA*	*VA*	*VIA*	*VIIA*
H 2.1						
Li 1.0	Be 1.2	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5

1. Label the columns of the table in Model 1 with their group numbers from the periodic table. For example, the column containing hydrogen is group IA.

   See Model 1.

2. Some of the elements in Model 1 have atoms that need only one or two electrons to fill their valence shell.

   a. Which columns in Model 1 contain these elements?

   Columns VIA and VIIA contain elements whose atoms only need one or two more electrons to fill their valence shell.

   b. Which of the elements in part *a* have atoms with the most pulling potential for an electron? Describe the subatomic structure in these atoms, which gives them this attractive force.

   The elements at the top of columns VIA and VIIA have the strongest attractive force from their nuclei because they have a high number of protons compared to other elements in their row and they have only a few electron shells filled, so the distance between the nucleus and a free electron will be small.

   c. Do these elements have a high electronegativity or a low electronegativity?

   The elements with the best chance of attracting an electron to themselves have high electronegativities.

3. Some of the elements in Model 1 have atoms with only one or two electrons in their valence shells. They can achieve a full valence shell by losing these electrons.

   a. Which columns in Model 1 contain these elements?

   Columns IA and IIA contain elements with atoms that need to give up one or two electrons to empty their valence shells.

   b. Which of the elements in part *a* will require the least amount of energy to remove an electron? Describe the subatomic structure in these atoms that allows an electron to be removed with very little energy.

   The elements at the bottom of these columns will require the least amount of energy to remove an electron. Although they have many protons, they also have several layers of electron shells. Due to shielding, the core charge of the atom is low and the distance between the nucleus and the valence electrons is large. Therefore, the electrons on the outermost shell are easy to remove.

   c. Do these elements have high electronegativities or low electronegativities?

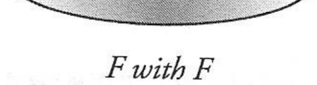
   Elements with atoms that easily lose their valence electrons have low electronegativities.

4. Suppose that a free electron was placed between two atoms. Predict the outcome of each contest by matching each set of atoms with a description. Be ready to share your reasoning with the class.

F with F	*Li with K*	Neither atom attracts the electron strongly. The electron is free to move about.
Li with O	*F with F*	Both atoms attract the electron strongly. The electron stays between the atom.
Li with K	*Li with O*	One atom attracts the electron strongly and pulls the electron towards itself.

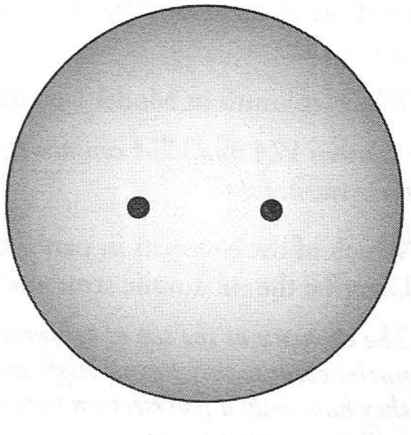
Model 2 – Types of Bonds

A



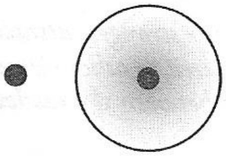
F with F
Both atoms attract the electrons strongly—covalent.

B



Li with K
Neither atom attracts the electron strongly—metallic.

C



Li with O
One atom easily takes an elecron from another—ionic.

5. The figures in Model 2 depict the valence electron distribution around bonded atoms. The black dots represent the nuclei of the two atoms that are bonded. The circles and ellipses represent the area where the bonded valence electrons could be. Darker shading indicates a higher probability of finding the electrons in that space.

   a. Which figure(s) in Model 2 indicates a sharing of electrons? Support your answer with evidence from Model 2.

   Figures A and B show atoms that are sharing electrons because the electron distribution area is around both nuclei.

   b. Which figure(s) in Model 2 indicates a transfer of electrons? Support your answer with evidence from Model 2.

   Figure C shows one atom with no electron distribution and the other atom with a tight, small electron distribution.

   c. Compare figures A and B in Model 2. In which case are the electrons more tightly held by the two nuclei of the bonded atoms? Support your answer with evidence from Model 2.

   The atoms in figure A are holding onto the electrons more tightly because the ellipse indicating the electron distribution is small and the darker area is between the nuclei. In figure B the electron distribution area indicated by the circle is much larger and the darker area is on the outside indicating a weak attractive force for the electrons.

6. These three situations are the results of the battles that took place in Question 4. Label the three figures in Model 2 with the contests from Question 4 and be prepared to explain your reasoning to the class.

   See Model 2.

Read This!

Ionic bonds are formed when one atom takes an electron from another atom. Ions are the result (one positive, one negative). They stick together because of opposite charges.

Covalent bonds are formed when both atoms have a strong attraction to the electron, so they share the electron. Neither atom has a charge.

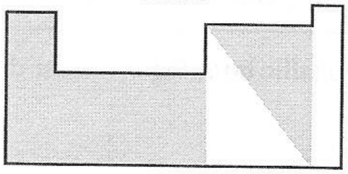
Metallic bonding occurs when neither atom has a strong attraction to the electrons.

7. Label the three figures in Model 2 with the three types of bonding described in the *Read This!* box.

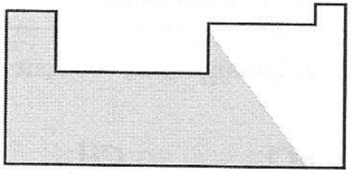
   See Model 2.

8. Bonds can be formed between atoms that come from the same region of the periodic table or between atoms that come from two different regions of the periodic table. For each of the bond types below, shade in one or two regions of the periodic table where atoms might come from to form that type of bond.

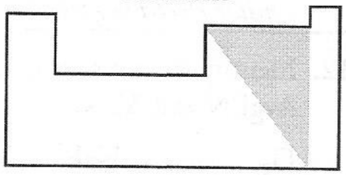
Ionic



Metallic



Covalent



Model 3 – Comparing Electronegativities

Substance	Electronegativity (EN)		AvgEN	ΔEN	Type of Bonding
	First atom	Second atom			
CsF (s)	0.7	4.0	*2.4*	*3.3*	Ionic
NaCl (s)	0.9	3.0	*1.95*	*2.1*	Ionic
NaI (s)	0.9	2.5	*1.7*	*1.6*	Ionic
Cs (s)	0.7	0.7	*0.7*	*0*	Metallic
Na (s)	0.9	0.9	*0.9*	*0*	Metallic
Mg (s)	1.2	1.2	*1.2*	*0*	Metallic
F_2 (g)	4.0	4.0	*4.0*	*0*	Covalent
HI (g)	2.1	2.5	*2.3*	*0.4*	Covalent
C (diamond, s)	2.5	2.5	*2.5*	*0*	Covalent

9. Calculate the average electronegativity (AvgEN) and the absolute difference in electronegativity (ΔEN) for the bonds in the substances listed in Model 3. Record these values in the appropriate columns in Model 3. Divide the work among group members.

   See Model 3.

10. Based on the data in Model 3, what combination of AvgEN and ΔEN values leads to each of the three bond types? Circle the appropriate word in each box.

	AvgEN			ΔEN		
Ionic	low	[✓ medium]	high	low	medium	[✓ high]
Metallic	[✓ low]	medium	high	[✓ low]	medium	high
Covalent	low	medium	[✓ high]	[✓ low]	medium	high

11. Explain your answers in Question 10 in terms of the analogies developed earlier in the activity (i.e., the atoms fighting for electrons).

    In ionic bonding, one atom pulls strongly on the electron, while the pull of the other atom is very weak. Therefore, the AvgEN will be somewhere between the extremes giving a medium result. Since the electronegativities are at the extremes, the ΔEN will be large.

    In metallic bonding, both atoms are weak in terms of attracting electrons. The AvgEN will be the average of two low numbers, giving a low result. The ΔEN will also be low since both of the atoms have similar electronegativities.

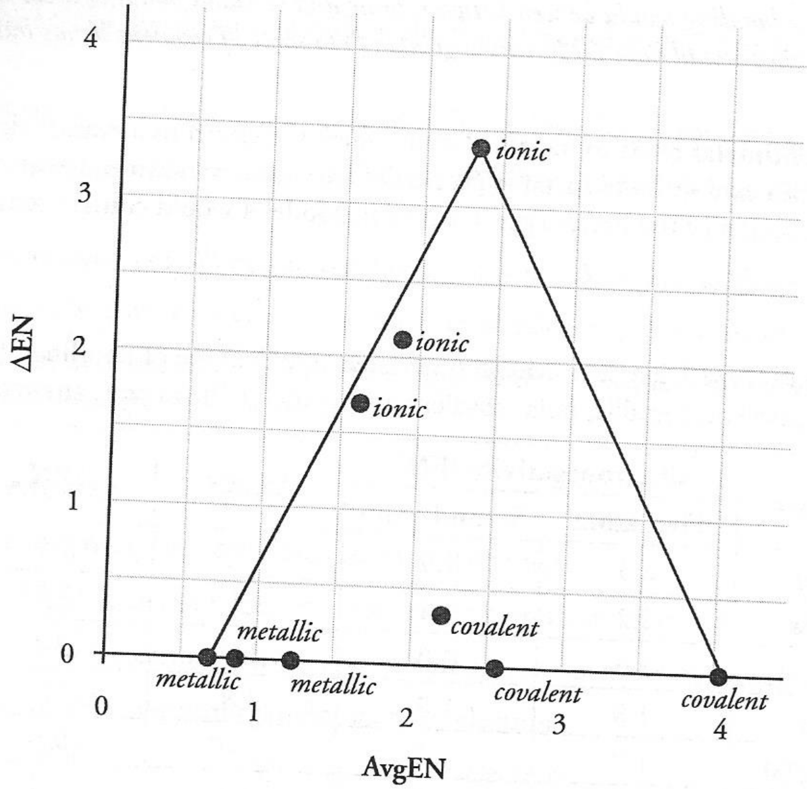
    In covalent bonding, both atoms are strong in terms of attracting electrons. The AvgEN will be the average of two high numbers, giving a high result. The ΔEN will be low since both of the atoms have similar electronegativities.

12. Identify the substances below as having ionic, covalent or metallic bonding based on their AvgEN and ΔEN.

O_2	NaF	KCl	CH_4	Fe
Covalent	*Ionic*	*Ionic*	*Covalent*	*Metallic*

Extension Questions

Model 4 – The Bond-Type Triangle



13. Plot each of the substances with known bond types from Model 3 on the graph in Model 4. Label each point with the type of bonding represented by each substance.

    See Model 4.

14. Use the points for the substances CsF, F_2 and Cs to generate a triangle on the graph in Model 4. Why were these points chosen to make the triangle?

    See Model 4.

    Fluorine has the highest electronegativity on the periodic table. Cesium has the lowest electronegativity on the periodic table. Therefore, these three combinations of their atoms represent the extreme cases for ionic, covalent and metallic bonding.

Read This!

Although as chemists (and students of chemistry) we would like the divisions between bonding types to be clear, they are more like points on a continuum—a two dimensional continuum. Many compounds have properties that are intermediate between the three bond types.

15. The term **polar covalent** refers to bonds where the electrons are not equally shared—there is a preference for one nucleus over the other. Discuss with your group what region of the Bond-Type Triangle in Model 4 would contain substances with polar covalent bonding.

    Polar covalent bonding would be seen between ionic and covalent bonding areas in the triangle. In other words, they would have ΔEN values greater than those of covalent bonds but less than those of ionic bonds.

16. The term **semimetal** refers to metallic bonds where the electrons are more tightly held. These substances will exhibit fewer metallic properties and more covalent properties. Discuss with your group what region of the Bond-Type Triangle in Model 4 would contain semimetallic substances.

    Semimetals would be seen in the boundary area between metallic and covalent bonding areas in the triangle.

17. Use the Bond-Type Triangle in Model 4 to determine the type of bonding of these substances. Use ionic, covalent, metallic, polar covalent and semimetallic as your answers.

Substance	**Electronegativity (EN)**		**AvgEN**	**ΔEN**	**Type of Bonding**
	First atom	**Second atom**			
ICl (s)	2.5	3.0	*2.75*	*0.5*	*Polar cov.*
MgO (s)	1.2	3.5	*2.35*	*2.3*	*Ionic*
GaAs (s)	1.6	2.0	*1.8*	*0.4*	*Semimetalic*
Si (s)	1.8	1.8	*1.8*	*0*	*Semimetallic*
Cd_3Mg (s)	1.7	1.2	*1.45*	*0.5*	*Metallic*
P_4O_7 (s)	2.1	3.5	*2.8*	*1.4*	*Polar cov.*
NCl_3 (l)	3.0	3.0	*3.0*	*0*	*Covalent*

Teacher Resources – Types of Bonds

Learning Objectives

1. Describe the role of the electron in each of the three types of bonding—ionic, covalent and metallic.
2. Identify the types of elements that would combine to form ionic, covalent and metallic bonds.
3. Use electronegativity values to identify the type of bonding between two atoms in a substance.

Prerequisites

1. Students should be able to determine the number of valence electrons in an atom.
2. Students should understand the Coulombic forces within the atom that contribute to electrons being tightly or loosely held by a nucleus.

Assessment Questions

1. Which of the following correctly describes ionic bonding?
   a. An atom of higher electronegativity gives an electron to an atom of lower electronegativity.
   b. An atom of lower electronegativity gives an electron to an atom of higher electronegativity.
   c. Two atoms of lower electronegativity share an electron.
   d. Two atoms of higher electronegativity share an electron.
2. When two nonmetal atoms bond, what type of bond will they most likely form?
   a. Ionic
   b. Covalent
   c. Metallic
   d. Two nonmetals will not bond.
3. For each of the substances below, identify the type of bonding between the atoms. Be prepared to justify your reasoning.

   SF_4 (g) $BaBr_2$ (s) Ca (s)

Assessment Target Responses

1. *b*
2. *b*
3. *SF_4(g) – Covalent* *$BaBr_2$(s) – Ionic* *Ca (s) – Metallic*

Teacher Tips

- In most cases, students in AP Chemistry will have had an introduction to bonding in a previous course. However, it is often the case that their understanding of the bond types is limited to rules they learned (e.g., ionic bonds form between metals and nonmetals). In this activity, students are asked to go back to the beginning and build an understanding of what is happening between the two atoms that are making a bond, and how electronegativity and Coulombic forces contribute to the type of bonding.
- When asking students to justify their reasoning to questions in this activity, make sure they speak to the Coulombic forces in the atoms and not just the electronegativity values in a table. This will help them when it comes to discussing the different properties that manifest because of bonding in substances.
- The electronegativity values in this activity are taken from the scale of electronegativity calculated by Linus Pauling, which seems to be the most common scale. Other scales include those developed by Robert S. Mulliken (absolute electronegativity), Louis Allred and Eugene Rochow (charge per unit area), and Leland Allen (AVEE model). Each is calculated in a slightly different way using different empirical properties. However, the trends seen in the values are very similar regardless of how they are calculated.

Alignment with AP Chemistry Framework

- **Essential Knowledge 2.C.1:** In covalent bonding, electrons are shared between the nuclei of two atoms to form a molecule or polyatomic ion. Electronegativity differences between the two atoms account for the distribution of the shared electrons and the polarity of the bond.
- **Essential Knowledge 2.C.2:** Ionic bonding results from the net attraction between oppositely charged ions, closely packed together in a crystal lattice.
- **Essential Knowledge 2.C.3:** Metallic bonding describes an array of positively charged metal cores surrounded by a sea of mobile valence electrons.

  Learning Objective 2.17 The student can predict the type of bonding present between two atoms in a binary compound based on position in the periodic table and the electronegativity of the elements.

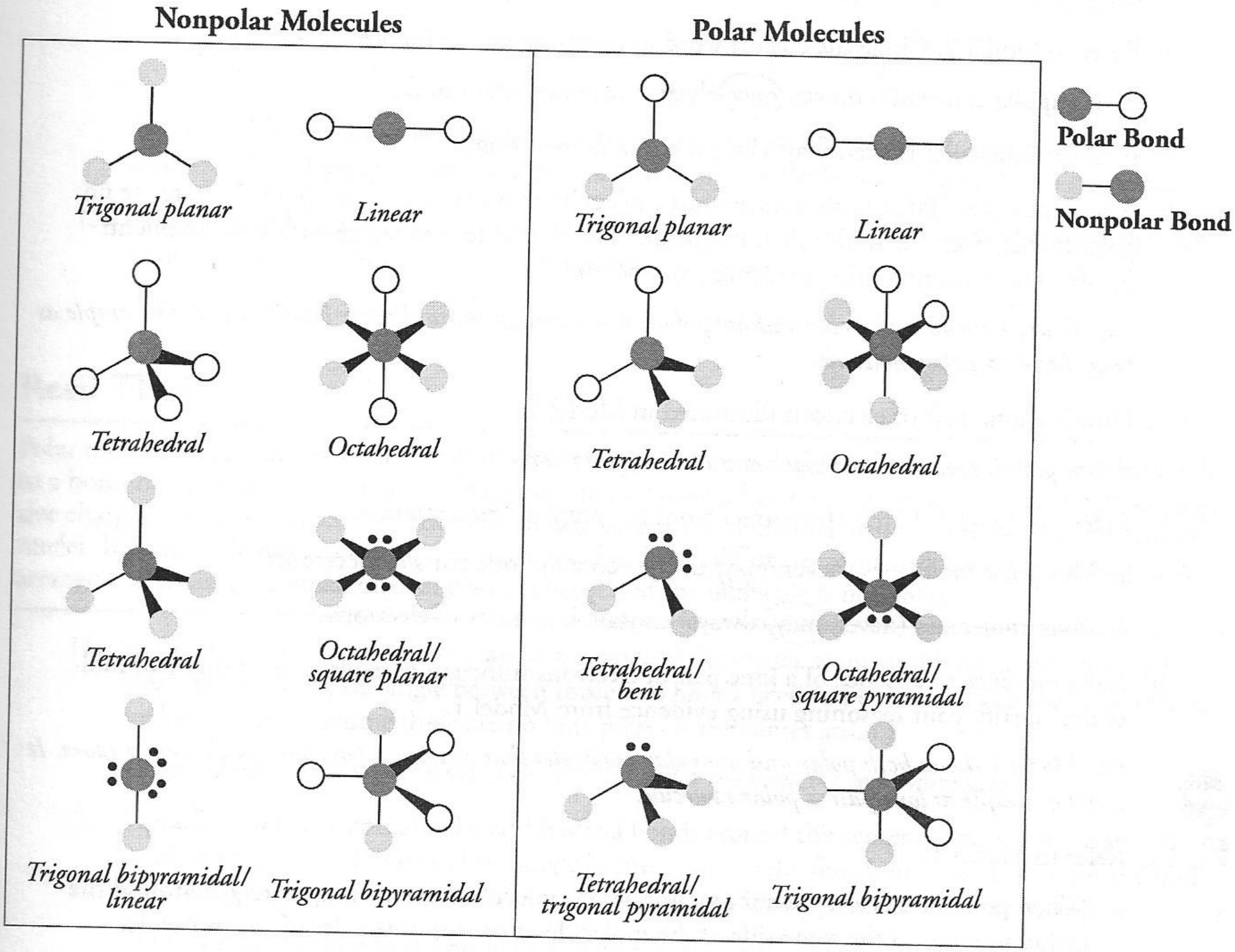
Polar and Nonpolar Molecules

What makes a molecule polar?

Why?

The physical properties of a substance are dictated in part by whether or not a molecule is polar. For example, oil and water do not mix because water is polar whereas oil is nonpolar. Another example is carbon dioxide and water. At room temperature, carbon dioxide is a gas while water is a liquid because carbon dioxide is nonpolar while water is polar. In this activity, you will explore the factors that contribute to a molecule's polarity or nonpolarity.

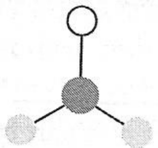
Model 1 – Examples of Nonpolar and Polar Molecules



1. Consider Model 1. How is a polar bond differentiated from a nonpolar bond?

   Polar bonds are indicated by an outer atom that is an open circle. Nonpolar bonds are indicated by an outer atom that is a shaded circle.

2. Formaldehyde has the chemical formula CH_2O, and it is trigonal planar. Draw this molecule using open and shaded circles as it might be shown in Model 1.



3. Label each diagram in Model 1 with the three-dimensional electronic shape that it represents.

   See Model 1.

4. According to Model 1, can the shape of a molecule explain polarity? Justify your reasoning.

   No, there are molecules of each type of shape represented in both the polar category and the nonpolar category. Therefore, shape alone cannot be the explanation for the polarity of a molecule.

5. Refer to Model 1. Circle the correct word to complete each sentence.

   a. Nonpolar molecules (never, [✓ may,] always) contain polar bonds.

   b. Polar molecules (never, [✓ may,] always) contain polar bonds.

6. A student states "Polar molecules are just molecules that contain polar bonds. If there are no polar bonds, then the molecule is nonpolar." Do you agree or disagree with this statement? Justify your reasoning using evidence from Model 1.

   No, Model 1 shows both polar and nonpolar molecules that contain polar bonds. It is not as simple as polar bonds = polar molecules.

7. How is a lone pair of electrons illustrated in Model 1?

   A lone pair is shown as two black dots on the center atom.

8. Refer to Model 1. Circle the correct word to complete the sentence.

   a. Nonpolar molecules (never, [✓ may,] always) contain lone pairs of electrons.

   b. Polar molecules (never, [✓ may,] always) contain lone pairs of electrons.

9. Is the presence or absence of a lone pair of electrons sufficient to explain the polarity of molecules? Justify your reasoning using evidence from Model 1.

   No, Model 1 shows both polar and nonpolar molecules that contain a lone pair on the center atom. It is not as simple as lone pair = polar molecule.

10. Refer to Model 1.

    a. When polar bonds are present in a nonpolar molecule, how are they arranged around the center atom—on the same side of the molecule or on opposite sides of the molecule?

    When polar bonds are present in a nonpolar molecule, the bonds are on opposite sides of the molecule.

    b. When polar bonds are present in a polar molecule, how are they arranged around the center atom—on the same side of the molecule or on opposite sides of the molecule?

    When polar bonds are present in a polar molecule, the bonds are on the same side of the molecule.

11. Refer to Model 1.

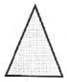
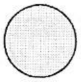
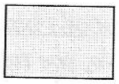
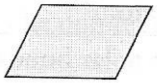
   a. When lone pairs of electrons are present in a nonpolar molecule, how are they arranged around the center atom—on the same side of the molecule or on opposite sides of the molecule?

   When lone pairs of electrons are present in a nonpolar molecule, they are on opposite sides of the molecule.

   b. When lone pairs of electrons are present in a polar molecule, how are they arranged around the center atom—on the same side of the molecule or on opposite sides of the molecule?

   When lone pairs of electrons are present in a polar molecule, they are on the same side of the molecule.

12. Consider the term "symmetry" as it is used in the English language. As a group, rank the following shapes from most symmetric to least symmetric.

Answers will vary. Group definitions may include the idea of reflection across a plane or planes of symmetry. For example, a cube has a high degree of symmetry whereas a chocolate chip cookie does not.

13. Which set in Model 1, the nonpolar molecules or polar molecules, contains molecules that are symmetric about multiple planes of symmetry?

The nonpolar molecules in Model 1 have the most symmetry.

Read This!

Polar molecules have an unequal distribution of charge around the molecule as a whole. This could be due to a bond being polar or a lone pair of electrons being present. Both would cause a concentration of negative charge on one side or in one area of the molecule due to an unequal distribution of electrons among nuclei. If a molecule has more than one polar bond or lone pair of electrons and they are symmetrically arranged, there is no unequal distribution of charge and the molecule is nonpolar.

14. Suppose a molecule contained two bonds around the center atom, and both those bonds were polar. What would the angle between those two bonds need to be for the molecule to be considered nonpolar? (Assume there are no lone pairs on the center atom.)

The two polar bonds would need to be 180° apart for the molecule to be nonpolar.

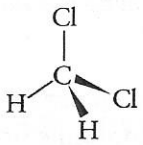
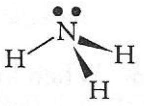
15. Suppose a molecule contained four identical bonds around the center atom, and all four of those bonds were polar. What would the angle between any of the four bonds need to be for the molecule to be considered nonpolar? (Assume there are no lone pairs on the center atom.)

The four polar bonds would need to be 109.5° apart (in a tetrahedral arrangement) or 90° apart (in a square planar arrangement) for the molecule to be nonpolar.

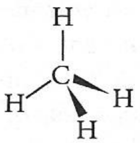
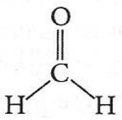
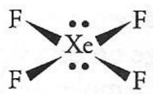
16. If a molecule contains only one polar bond and no lone pairs, is there an arrangement that will make that molecule nonpolar? Justify your reasoning.

With only one polar bond the molecule will certainly be polar. There is no other polar bond to create symmetry in the molecule to make it nonpolar.

17. Fill in the table below for each molecule to determine if the molecule is polar or nonpolar. You may want to refer to a table of electronegativity values.

Name	**Dichloromethane**	**Carbon dioxide**	**Ammonia**
Structure		$O=C=O$	
Does the molecule have polar bonds? If yes, which ones?	*Yes, the C—Cl bonds are polar.*	*Yes, the C═O bonds are polar.*	*Yes, the N—H bonds are polar.*
Does the molecule have lone pairs on the center atom?	*No*	*No*	*Yes*
If there are polar bonds and/or lone pairs, are they symmetric?	*No, the two C—Cl bonds are not 180° apart.*	*Yes, the two C═O bonds are 180° apart.*	*No, there is only one lone pair.*
Is the molecule polar or nonpolar?	*Polar*	*Nonpolar*	*Polar*

18. Draw the three-dimensional structures for each molecule. Fill in the table for each molecule to determine if the molecule is polar or nonpolar.

Name	**Methane (CH_4)**	**Formaldehyde (CH_2O)**	**Xenon tetrafluoride (XeF_4)**
Structure			
Does the molecule have polar bonds? If yes, which ones?	*No*	*Yes, the C═O bond is polar.*	*Yes, the Xe—F bonds are polar.*
Does the molecule have lone pairs on the center atom?	*No*	*No*	*Yes*
If there are polar bonds and/or lone pairs, are they symmetric?	*NA*	*No, there is only one polar bond.*	*Yes, the four polar bonds are 90° apart, and the two lone pairs are 180° apart.*
Is the molecule polar or nonpolar?	*Nonpolar*	*Polar*	*Nonpolar*

19. Determine if the following molecules are polar or nonpolar.

a. Carbon tetrafluoride (CF_4) *Nonpolar*

b. Water (H_2O) *Polar*

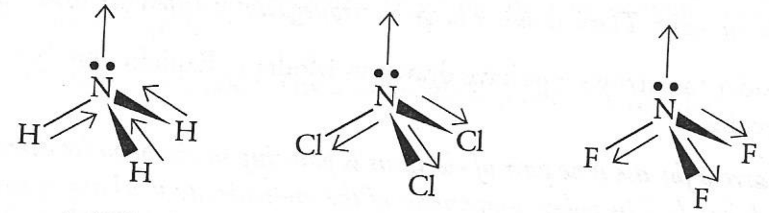
c. Sulfur dioxide (SO_2) *Polar*

d. Phosphorous pentachloride (PCl_5) *Nonpolar*

e. Hydrogen sulfide (H_2S) *Polar*

Extension Questions

Model 2 – A Series of Polar Molecules



Dipole Moment 1.42 D 0.60 D 0.23 D

20. The polarity of a molecule can be quantified as the dipole moment. The dipole moment is either found indirectly through experiment or calculated theoretically. The dipole moment is measured in debyes.

    a. What is the abbreviation for the unit "debye"?

    The debye is abbreviated with a "D."

    b. Which molecule in Model 2 is the most polar according to the dipole moments given?

    The NH_3 molecule is the most polar because it has the largest dipole moment.

21. Discuss as a group the dipole moment values provided in Model 2. Propose some possible explanations for the changes in the dipole moments between the three molecules. In particular note anything that seems unusual in the data.

    Answers will vary. Students should note that the shape and number of lone pairs on all three molecules are the same. However, the polarity of the bonds would change because of the outer atoms. Students will probably be uncomfortable with the fact that the molecule containing fluorine (the most electronegative element) results in the least polar molecule. The NH_3 molecule has the largest dipole moment because of the large difference in electronegativity between the N and H atoms and the direction of the polarity in the bond.

22. The dipole moment of a bond or molecule is often represented with an arrow that points toward the more negative side of the bond.

    a. Determine which bonds in Model 2 are polar bonds using a table of electronegativity values. A large difference in electronegativity is characteristic of a polar bond.

    The N—H and N—F bonds would be considered polar. The N—Cl bond is slightly polar, but would not qualify under most "rule of thumb" systems.

    b. For any bond shown in Model 2 that is significantly polar, draw an arrow next to the bond to show the direction of polarity.

    See Model 2.

23. The lone pairs in a molecule also provide a dipole. Draw an arrow that points away from the center atom for any lone pairs on the molecules in Model 2.

    See Model 2.

24. Consider the arrows you have drawn in Model 2. Explain why NH_3 is the most polar of the three molecules.

All of the arrows representing polar bonds and lone pairs point in the same direction. All of the components that cause the molecule to be polar are working in the same direction to cause an overall large dipole moment. There is also a large electronegativity difference between N and H.

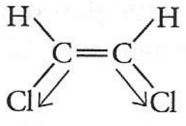
25. Consider the arrows you have drawn in Model 2. Explain why NF_3 is the least polar of the three molecules.

The arrow for the lone pair of electrons is pointing in the opposite direction from the three polar N—F bonds. The polar components of the molecule are working against each other, resulting in only a slightly polar molecule and a small dipole moment. Also, the electronegativity difference between N and F is not huge.

26. The phosphorus trifluoride molecule (PF_3) has a dipole of 1.03 D. Compare this molecule to the nitrogen trifluoride molecule in Model 2. Propose a reason for the larger dipole in the molecule containing phosphorus.

The P—F bond is more polar than the N—F bond, owing to the larger electronegativity differences between P and F. Therefore, the bond polarities are able to overcome the opposite direction of pull from the lone pair and make the PF_3 molecule very polar.

27. Rank the following molecules in order of polarity from least to most. Use arrows on each molecule to support your answer.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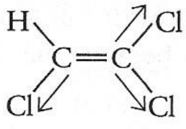
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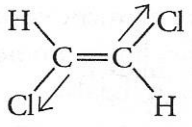
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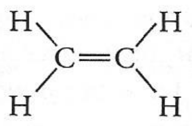
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When the arrows "add," or point in the same direction, the molecule is very polar. When the arrows "cancel" or point in opposite directions, the molecule is less polar or nonpolar.

28. Select the molecule in each pair that has the largest dipole moment. Include diagrams and complete sentences to justify your reasoning.

a. CS_2 vs. [✓ SO_2]

The CS_2 molecule is linear while the SO_2 molecule is bent trigonal-planar. Since the SO_2 molecule contains a single lone pair on the center atom, it has the larger dipole moment. The CS_2 molecule is symmetric, while the SO_2 molecule is not.

b. [✓ H_2O] vs. OF_2

The bond polarity in H_2O is shifting the electron density towards the center atom, working with the lone pairs, while the bond polarity in OF_2 is shifting the electron density away from the center atom, opposite the lone pairs.

c. CF_4 vs. [✓ SF_4]

The CF_4 molecule is tetrahedral with no lone pairs. The SF_4 molecule is a see-saw that includes a lone pair on the center atom. The CF_4 molecule is symmetric, while SF_4 is not.

Teacher Resources – Polar and Nonpolar Molecules

Learning Objectives

1. Determine if a molecule is polar or nonpolar by considering the arrangement of polar bonds and lone pairs in three-dimensional space.
2. Apply the concept of symmetry to explain why a molecule is polar or nonpolar.

Prerequisites

1. Students should be able to draw Lewis dot-diagrams for simple covalent molecules.
2. Students should be able to use electronegativity data to determine if a bond is polar or nonpolar. For the purposes of this activity, a bond between carbon and hydrogen is considered nonpolar.
3. Students should be able to determine the shape of a molecule based on VSEPR theory.

Assessment Questions

1. Which of the molecules below is polar?
   - *a.* CF_4
   - *b.* CO_2
   - *c.* SF_4
   - *d.* RnF_4
2. Which statement below correctly explains why BF_3 is nonpolar?
   - *a.* The bonds between boron and fluorine are nonpolar.
   - *b.* The bonds between boron and fluorine are polar, but symmetrically arranged.
   - *c.* The lone pairs are symmetrically arranged.
   - *d.* None of the above.
3. Molecules of AsF_3 are polar while molecules of AsF_5 are nonpolar. Use a symmetry argument to explain why.

Assessment Target Responses

1. *c*
2. *b*
3. The AsF_3 molecule is trigonal pyramidal, which contains a single lone pair of electrons. Since there is not a second lone pair of electrons to be symmetric with the first, the molecule is polar. The AsF_5 molecule is trigonal bipyramidal and contains no lone pairs. The bonds in both molecules are polar, but they are symmetrically arranged in AsF_5.

Teacher Tip

- It is recommended that students have three-dimensional models available for this activity. Many times students do not see the symmetry of tetrahedral or trigonal bipyramidal molecules until they are able to manipulate the models in their hands.

Alignment with AP Chemistry Framework

- **Essential Knowledge 2.C.4:** The localized electron bonding model describes and predicts molecular geometry using Lewis diagrams and the VSEPR model.

  Learning Objective 2.21 The student is able to use Lewis diagrams and VSEPR to predict the geometry of molecules, identify hybridization, and make predictions about polarity.

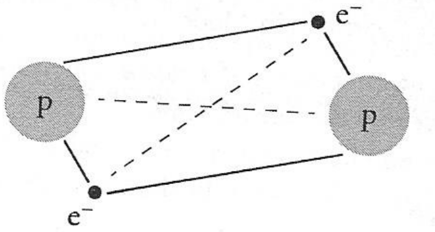
Properties of Covalent Bonds

What factors determine the length and strength of a covalent bond?

Why?

Many of the chemical and physical properties of a substance are determined by the strength and/or length of the bonds within that substance. It is fairly easy to find values for these properties in your textbook or on the Internet. It is even more helpful however to understand what makes a bond stronger or weaker than another bond. These trends in bond length and energy will be explored in this activity.

Model 1 – Attractive and Repulsive Forces



e^- = *Electron*
p = *Proton*

1. Two atoms are illustrated in Model 1 (not to scale). Identify the element to which the atoms belong.

   Both atoms are hydrogen atoms.

2. Consider the attractive and repulsive forces that would exist if the atoms in Model 1 were to approach each other by random motion.

   a. Draw a dashed line to represent any repulsive forces between similarly charged particles.

   See Model 1.

   b. Draw a solid line to represent any attractive forces between oppositely charged particles.

   See Model 1.

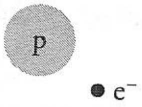
3. In order for a bond between atoms to be stable, how should the attractive forces compare to the repulsive forces?

   For a bond to be stable, the attractive forces must exceed the repulsive forces.

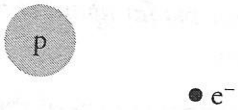
4. Recall that the potential energy of the system is decreased when attractive forces are maximized.

   a. Which situation below would have the lowest potential energy? Justify your reasoning.

   I.



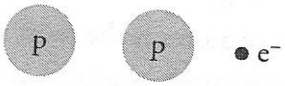
   II.



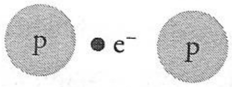
   Situation I would have the lowest potential energy because the electron is closer to the proton which would increase the attractive force between the particles.

   b. Which situation below would have the lowest potential energy? Justify your reasoning.

   I.

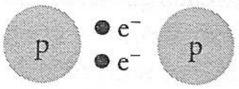


   II.

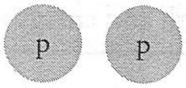


   Situation II would have the lowest potential energy because the total distance between the electron and the two protons is less than the total distance in situation 1.

5. Draw a diagram similar to that in Model 1 showing where the electrons would be in relationship to the nuclei when the attractive forces in the system are maximized.



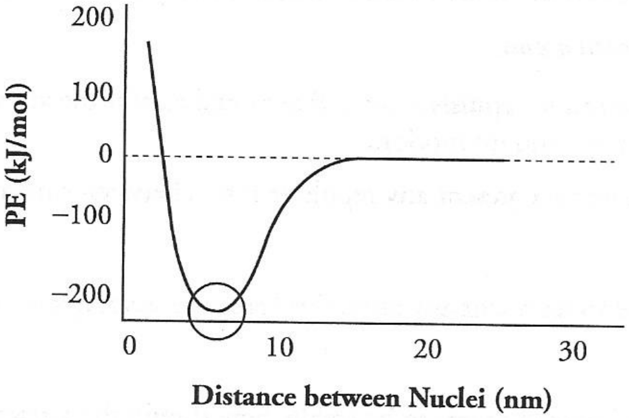
6. Draw a diagram similar to that in Model 1 showing where the nuclei would be when the repulsive forces in the system are maximized.



7. Attractive forces are written using negative potential energy values. Explain why this is reasonable in terms of the energy of the system of particles in Model 1.

Forces of attraction decrease the total potential energy of a system. Therefore, the energy values of attraction are written as negative because they decrease the total.

Model 2 – A Bond Energy Curve



8. The graph in Model 2 shows the changes in potential energy of a two-atom system as the distance between nuclei changes.

   a. Consider the potential energy of the system when the atoms are more than 15 nm apart. Describe the system's potential energy in terms of attractive and repulsive forces.

   When the atoms are too far apart, there are no attractive or repulsive forces so the potential energy of the system is zero.

   b. Consider the potential energy of the system when the atoms are less than 5 nm apart. Describe the system's potential energy in terms of attractive and repulsive forces.

   When the nuclei are very close together, the repulsive forces dominate so the potential energy of the system increases and is positive.

9. Circle the place on the graph where the system of atoms is the most stable. Justify your reasoning.

See Model 2. The system of atoms would be most stable when it is at the lowest potential energy point.

Read This!

When atoms bond, they are not still. Bonds are more like frictionless springs that have been stretched and released. The atoms vibrate, getting closer and further apart rhythmically. Therefore, it is difficult to determine a "bond length" for a given system of atoms. It is possible, however, to determine the most stable distance between atoms. This is sometimes tabulated as the **average bond length** in chemistry textbooks. Keep in mind that the atoms likely vibrate at approximately that distance.

10. According to the graph in Model 2, what is the approximate average bond length for the system of atoms illustrated?

    The average bond length is about 6 nm.

11. If the atoms in Model 2 were at their most stable bond length, how much energy would be needed to separate one mole of atom pairs completely?

    To separate the atoms there would need to be an addition of about 210 kJ/mole of energy.

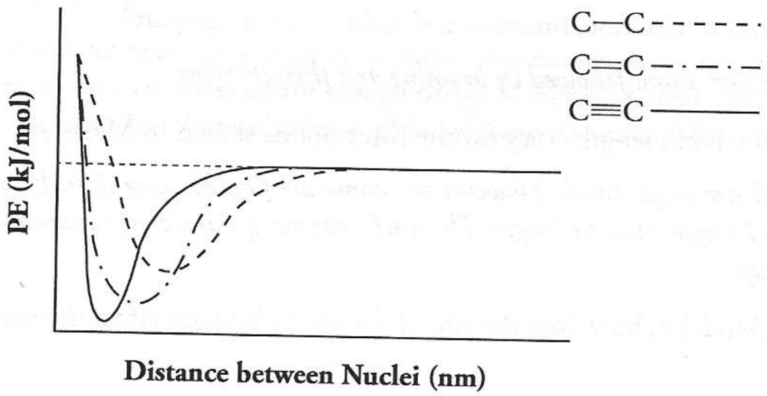
12. According to Model 2, how much energy would be released when the two moles of atoms formed bonds to make one mole of bonded atom pairs?

    When the atoms formed a stable bond, about 210 kJ/mole of energy would be released.

13. Based on your answer in Question 12, how much energy would be released when one bond formed between two atoms?

$$\frac{210\,\frac{kJ}{mole}}{6.02\times 10^{23}\,\frac{bonds}{mole}} = 3.49\times 10^{-22}\,\frac{kJ}{bond}$$

Model 3 – Comparing Potential Energy Curves



14. Model 3 illustrates the potential energy curves for three different bonds. What three bonds are illustrated?

    The bond energy curves for single, double and triple bonds between carbon atoms are illustrated in Model 3.

15. Which of the three bonds has the shortest average bond length?

The triple bond has the shortest average bond length.

16. Which of the three bonds has the smallest bond energy?

The single bond has the smallest bond energy.

17. Compare the potential energy curves in Model 3. When a higher order bond forms between atoms, is the bond strengthened or weakened? Justify your reasoning.

When a higher order bond is formed, the bond is strengthened because the energy needed to break the bond is increased.

18. Two oxygen atoms can form a single bond or a double bond between them. Complete the table below with either O—O or O=O in the far left column.

Bond	Average Bond Length (pm)	Average Bond Energy (kJ/mole)
O—O	148	145
O=O	121	498

Model 4 – The Effect of Atom Size

Bond	Average Bond Length (pm)	Average Bond Energy (kJ/mole)
Cl—Cl	199	243
Br—Br	228	193
I—I	267	151

19. How do the sizes of chlorine, bromine and iodine atoms compare?

Iodine is the largest atom, followed by bromine and then chlorine.

20. Explain why the bond lengths vary for the three bonds shown in Model 4.

All of the bonds are single bonds. However the atoms are not the same sizes. Because iodine atoms are larger, the bond length must be longer. The nuclei cannot get any closer because there are more electron shells in the way.

21. According to Model 4, how does the size of the atoms bonded affect the strength of the bond formed?

As the size of the atoms increases, the bond strength decreases.

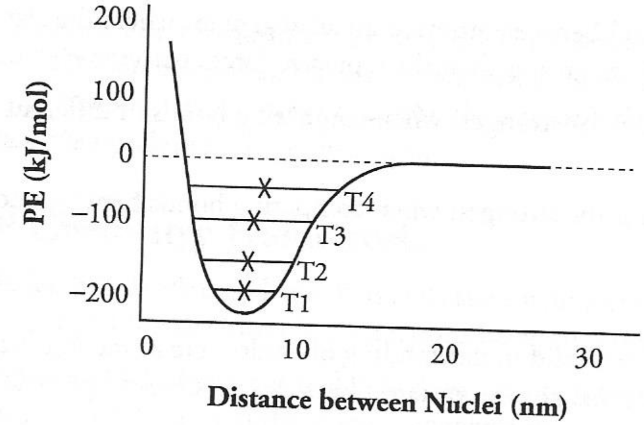
22. Predict which bond below would have the highest average bond energy. Justify your reasoning.

H—N H—O H—F

The H—F bond would have the highest average bond energy because the fluorine atom is the smallest. This allows the bond length to be shorter, increasing attractive forces. ***Note:*** *The actual bond energies are 314 kJ/mole, 428 kJ/mole and 568 kJ/mole, respectively.*

Extension Questions

Model 5 – Effect of Temperature



23. When the temperature of a substance increases, the bond vibrations get more extreme. Model 4 illustrates the minimum and maximum bond length during a vibration for four different temperatures. Which temperature is the highest temperature?

    The temperature represented by T4 is the highest temperature.

24. Explain why it is possible in most cases to break a covalent bond by increasing the temperature.

    If the temperature increases such that the bond vibrates to the point that there are no attractive forces (greater than 15 nm distance), the bond will be broken.

25. Use a ruler to find the midpoint of each temperature line in Model 5. Mark the midpoints with an X. What do these midpoints represent in terms of bond properties?

    See Model 5. The midpoints of each line represent the average bond length at that temperature.

26. Explain why most substances exhibit thermal expansion—the volume of a sample increases when the temperature increases.

    As the temperature increases, the average bond length (represented by the midpoint of each temperature line) increases because atoms attain enough energy to migrate farther away from each other. If the bond lengths increase, then the total volume of the substance increases. This is thermal expansion.

Teacher Resources – Properties of Covalent Bonds

Learning Objectives

1. Describe a stable bond between atoms as an arrangement where the attractive forces between electrons and nuclei are greater than the repulsive forces between electrons or nuclei.
2. Predict which bond is the strongest when comparing bonds of different order between similar atoms.
3. Predict which bond is the strongest when comparing bonds between atoms of different sizes.

Prerequisites

1. Students should have a solid understanding of coulombic attraction including how attractive or repulsive forces may change with distance between the charged particles and magnitude of the charges on the particles.
2. Students should understand that stable bonds reduce the potential energy of the system of atoms and therefore release energy when bonds are formed.
3. Students should be able to make predictions about atomic size based on periodic trends.
4. Students should understand that covalent bonds are formed when the electron orbitals of two atoms overlap and the electrons are shared.

Assessment Questions

1. Which statement below correctly explains why carbon and fluorine atoms form a stronger bond than carbon and bromine atoms?

   a. Fluorine atoms are smaller than bromine atoms.

   b. Fluorine atoms are more electronegative than bromine atoms.

   c. Fluorine atoms have fewer protons than bromine atoms.

   d. Fluorine atoms form a higher order bond with carbon than bromine atoms.

2. Predict which of the bonds below would be strongest.

   a. N—N

   b. N═N

   c. N≡N

   d. All bonds would be the same strength.

3. Discuss the formation of a stable bond in terms of the total attractive and repulsive forces between two atoms.

Assessment Target Responses

1. *a*
2. *c*
3. *When two atoms approach one another, there are repulsive forces between like-charged particles (electron to electron and proton to proton), and there are attractive forces between oppositely-charged particles (electrons to protons). For a bond to be stable, the attractive forces in the two-atom system must be greater than the repulsive forces in the system.*

Alignment with AP Chemistry Framework

- **Essential Knowledge 5.C.1:** Potential energy is associated with a particular geometric arrangement of atoms or ions and the electrostatic interactions between them.

  Learning Objective 5.8 The student is able to draw qualitative and quantitative connections between the reaction enthalpy and the energies involved in the breaking and formation of chemical bonds.

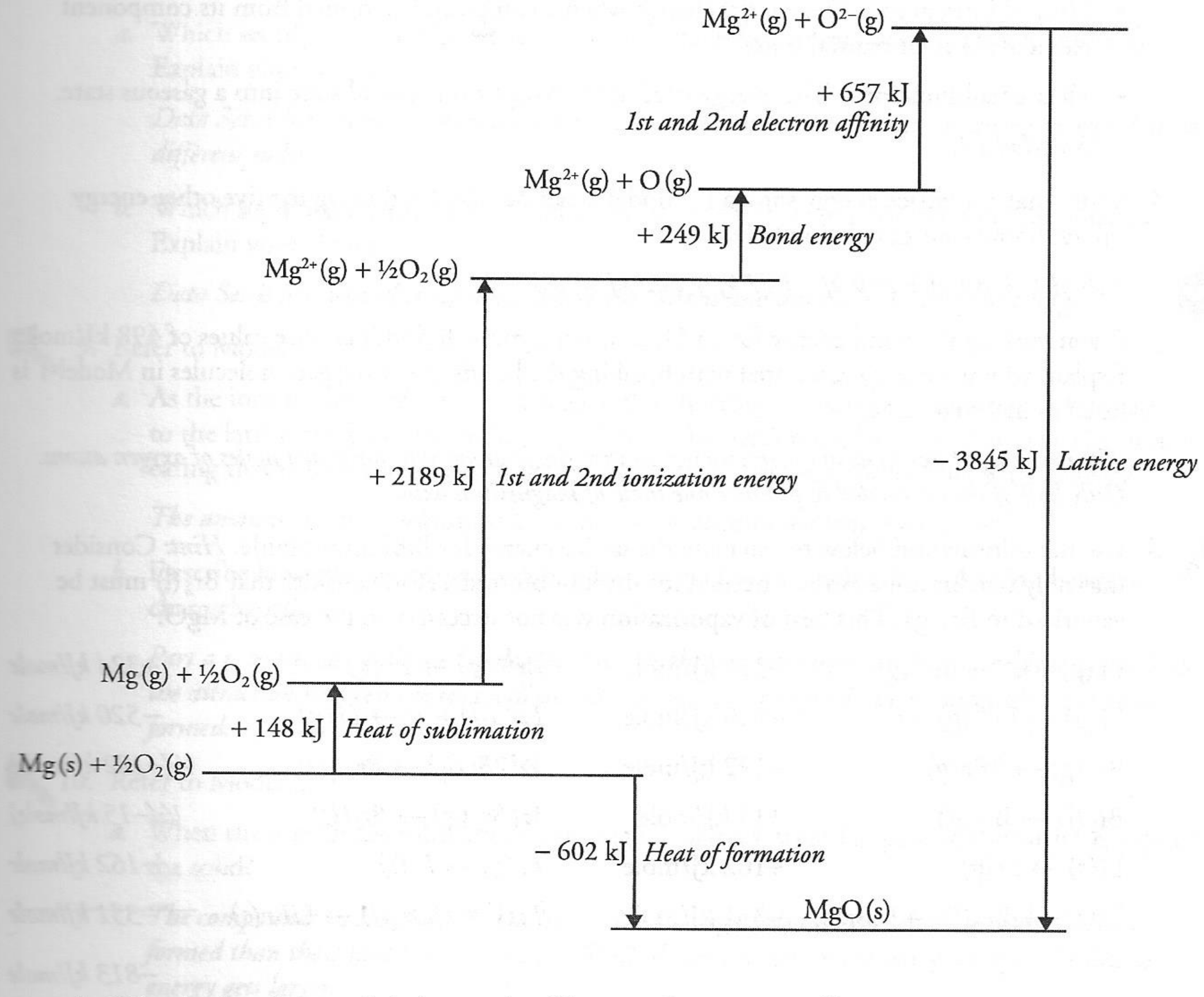
Lattice Energy

How strong are the ionic bonds in an ionic solid?

Why?

When comparing the strengths of covalent bonds we can use bond energy tables to estimate the energy released when a particular bond is formed. The more energy that is released, the stronger, or more stable the bond. Ionic bonds have a similar quantity called **lattice energy**. Lattice energy is defined as the change in energy when ions in their gaseous state form an ionic solid. It is very difficult to directly measure lattice energies for ionic substances, so they are usually theoretically calculated from other data. In this activity, we will look at the variables that determine the magnitude of the lattice energy.

Model 1 – The Born-Haber Cycle



1. What ionic substance is being used to illustrate the concept of lattice energy in Model 1?

   The lattice energy of magnesium oxide is illustrated in Model 1.

2. According to the *Why?* box on the previous page, what is the definition of lattice energy? Label the arrow in Model 1 that represents lattice energy.

   The lattice energy is the change in energy when ions in their gaseous state form an ionic solid.

   See Model 1.

3. The lattice energy is theoretically calculated from five other energies. They are listed below with their definitions. Label the remaining arrows in Model 1 with these five energies.

   - 1st and 2nd electron affinity—The energy needed to add two electrons to an atom to form an anion.
   - 1st and 2nd ionization energy—The energy needed to remove an electron from an atom to form a cation.
   - Bond energy—The energy needed to break a covalent bond between atoms.
   - Heat of formation—The energy change when a compound is formed from its component elements in their natural state.
   - Heat of sublimation—The energy needed to change from a solid state into a gaseous state.

   See Model 1.

4. Verify that the lattice energy shown in Model 1 can be calculated using the five other energy values. Show your calculation here.

   148 kJ + 2189 kJ + 249 kJ + 657 kJ + 602 kJ = 3845 kJ

5. If you look up the bond energy for an O_2 molecule, you will find literature values of 498 kJ/mole. Explain why the energy associated with breaking the bonds in the oxygen molecules in Model 1 is listed as half that value.

   The breaking of one mole of oxygen molecules into single atoms will form two moles of oxygen atoms. Only half of that is needed to produce one mole of magnesium oxide.

6. Use the information below to calculate the lattice energy for lithium bromide. *Hint:* Consider that only one bromine atom is needed for lithium bromide. Also consider that Br_2 (l) must be vaporized to Br_2 (g). This heat of vaporization was not necessary in the case of MgO.

$Br(g) + e^- \rightarrow Br^{1-}(g)$	−324 kJ/mole	$Br^{1-}(g) \rightarrow Br(g) + e^-$	*+324 kJ/mole*
$Li(g) \rightarrow Li^{1+}(g) + e^-$	+520 kJ/mole	$Li^{1+}(g) + e^- \rightarrow Li(g)$	*−520 kJ/mole*
$Br_2(g) \rightarrow 2Br(g)$	+192 kJ/mole	$\frac{1}{2}(2Br(g) \rightarrow Br_2(g))$	*½(−192 kJ/mole)*
$Br_2(l) \rightarrow Br_2(g)$	+15 kJ/mole	$\frac{1}{2}(Br_2(g) \rightarrow Br_2(l))$	*½(−15 kJ/mole)*
$Li(s) \rightarrow Li(g)$	+162 kJ/mole	$Li(g) \rightarrow Li(s)$	*−162 kJ/mole*
$Li(s) + \frac{1}{2}Br_2(l) \rightarrow LiBr(s)$	−351 kJ/mole	$Li(s) + \frac{1}{2}Br_2(l) \rightarrow LiBr(s)$	*−351 kJ/mole*
			−813 kJ/mole

7. Consider the definition of lattice energy. Would you predict that lattice energies are always exothermic? Justify your reasoning.

   Yes, consider that energy is required to melt most ionic compounds, or to destroy their crystal lattices. By Hess's law then, energy must be released when an ionic solid is formed from its elements.

Model 2 – Atom Size and Charge

Data Set A

	Lattice energy (kJ/mol)
LiCl	−830
NaCl	−770
KCl	−700
RbCl	−680
CsCl	−660

Data Set B

	Lattice energy (kJ/mol)
NaCl	−770
$MgCl_2$	−2530
Na_2O	−2570
MgO	−3930
Al_2O_3	−15270

8. Consider the data presented in Model 2.

   a. Which set of data could be analyzed to show the effect atomic size has on lattice energy? Explain your choice.

   Data Set A lists several compounds where the metal atoms in the lattice are all +1 charge, but have different radii.

   b. Which set of data could be analyzed to show the effect ion charge has on lattice energy? Explain your choice.

   Data Set B lists several compounds where the cations and anions have different charges.

9. Refer to Model 2.

   a. As the ions in the solid lattice get bigger, thus making the bond length longer, what happens to the lattice energy of the solid? *Note:* Ignore the sign on the lattice energy. The sign is indicating that energy is released. You are interested in the magnitude of the lattice energy.

   The amount of energy released is less as the metal atom in the lattice gets larger.

   b. Describe how your answer in part *a* relates to the law of Coulombic attraction between charged particles?

   Part a is consistent with the Coulombic law. As the ion gets larger, and the bond length gets larger, the attraction between the ions will decrease. Thus, less energy will be released when the bond is formed.

10. Refer to Model 2.

    a. When the ions in the solid lattice have higher charges, what happens to the lattice energy of the solid?

    The compounds in Data Set B that have +1/−1 charges release less energy when the lattice is formed than those that have +2/−2 or +3/−2. As the charges on the ions get larger, the lattice energy gets larger.

    b. Describe how your answer in part *a* relates to the law of Coulombic attraction between charged particles.

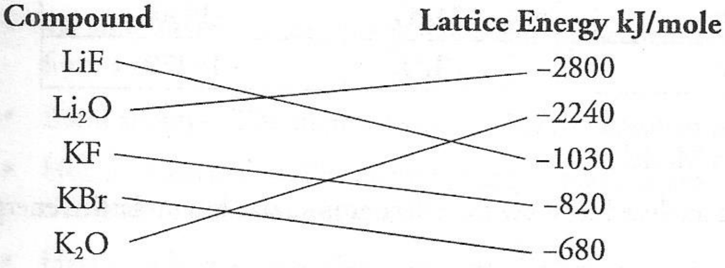
    Part a is consistent with the Coulombic law. As the ion charges get larger, the attraction between the ions is stronger. Thus, more energy will be released when the bond is formed.

STOP

11. Work individually on this question and then discuss your answers as a group. Which compound in each row would have the larger lattice energy? Be prepared to justify your reasoning.

MgO	$MgCl_2$	*MgO—the charges are larger (+2/–2 vs. +2/–1)*
$MgCl_2$	MgF_2	*MgF_2—the fluoride ion is smaller than the chloride ion*
MgO	CaO	*MgO—the magnesium ion is smaller than the calcium ion*
$AlCl_3$	Al_2O_3	*Al_2O_3—the charges are larger (+3/–2 vs. +3/–1)*

12. Match the ionic compounds below to their lattice energy.



Extension Questions

13. The lattice energy (attractive force) of an ionic solid can be approximated using the Coulombic force equation shown below. Use your understanding of lattice energy and Coulombic attraction to answer the following.

$$F = k\frac{q_1 q_2}{r^2}$$

   a. Identify each of the variables in the equation.

F	k	q_1 and q_2	r
force	*constant*	*charges*	*distance between ions*

   b. When you calculate the force between a positive and negative ion, will the force be positive or negative? Explain your reasoning.

   When the charges are multiplied, they will result in a negative number. There are no other values in the equation that are negative, so the resulting force will be negative.

   c. When you calculate the force between two negative ions will the force be positive or negative. Explain your reasoning.

   When the charges are multiplied, they will result in a positive number. There are no other values in the equation that are negative, so the resulting force will be positive.

   d. How are attractive and repulsive forces distinguished when calculating forces?

   Attractive forces are given a negative force value and repulsive forces are given a positive force value.

14. Most heats of formation for ionic compounds are exothermic—energy is released when the compound forms from its elements in their natural state. However, some are endothermic overall.

   a. Refer to Model 1. What must be true about the relative magnitudes of the energies involved in that model to make a heat of formation for an ionic compound endothermic?

   The lattice energy must be smaller than the sum of the energies needed to turn the elements in their natural state into gaseous ions (sublimation, vaporization, ionization and electron affinity energies).

   b. Would an ionic compound with an endothermic heat of formation be as shelf stable (can be stored for a long time without decomposing) as an ionic compound with an exothermic heat of formation? Explain your reasoning.

   The compound would most likely not be shelf stable if it had a heat of formation that was endothermic. This means the elements in their natural state are more stable than the compound. This would mean decomposition was thermodynamically favorable.

Teacher Resources – Lattice Energy

Learning Objectives

1. Define lattice energy as the energy released when gaseous ions form a solid crystal lattice.
2. Use the Born-Haber cycle to calculate the lattice energy of a solid ionic compound from other heats of reaction provided in the question.
3. Determine which of two ionic compounds will have the larger lattice energy based on the size and charges of the ions involved.

Prerequisites

1. Students should have a solid understanding of Coulombic attraction and be able to explain how the strength of an attractive force between oppositely charged ions changes with distance and charge.
2. Students should have working definitions of the following—sublimation, vaporization, bond energy, electron affinity, ionization energy, heat of formation—and be able to match these words to reactions representing these changes in energy.
3. Students should be able to use Hess's law to find the heat of a reaction using other heats of reactions provided in the question.

Assessment Questions

1. In which of the following reactions would the energy change be equal to the lattice energy of the product?
   a. $Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$
   b. $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$
   c. $Na(g) + Cl(g) \rightarrow NaCl(s)$
   d. $Na^{1+}(g) + Cl^{1-}(g) \rightarrow NaCl(s)$
2. Which ionic compound would have the larger lattice energy: MgF_2 or CaF_2? Justify your reasoning.
3. Which ionic compound would have the larger lattice energy: $SrCl_2$ or SrO? Justify your reasoning.

Assessment Target Responses

1. *d*
2. *MgF_2 will have the larger lattice energy because the magnesium ion is smaller than the calcium ion. The distance between charged particles will be less, so the strength of Coulombic attraction will be greater.*
3. *SrO will have the larger lattice energy because the charges in SrO are larger than in $SrCl_2$ (+2/–2 versus +2/–1). The higher charged particles will have a stronger Coulombic attraction for one another.*

Teacher Tip

- The definition of lattice energy for ionic compounds seems to be controversial. Some texts and websites define it as the energy released when gaseous ions come together to form an ionic solid. Others define it as the energy needed to separate an ionic solid into gaseous ions. Make sure students understand that these are the same definitions, just opposite signs on the energy value. This is especially important if your text refers to the lattice energy in the opposite way of this activity.

Alignment with AP Chemistry Framework

- **Essential Knowledge 2.C.2:** Ionic bonding results from the net attraction between oppositely charged ions, closely packed together in a crystal lattice.
- **Essential Knowledge 2.D.1:** Ionic solids have high melting points, are brittle, and conduct electricity only when molten or in solution.

  Learning Objective 2.23 The student can create a representation of an ionic solid that shows essential characteristics of the structure and interactions present in the substance.

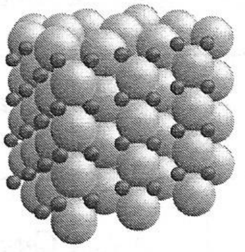
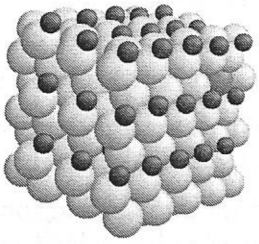
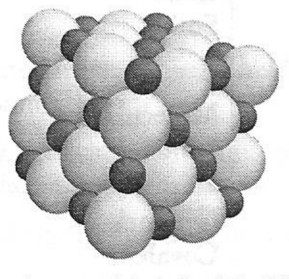
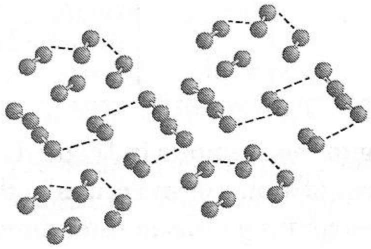
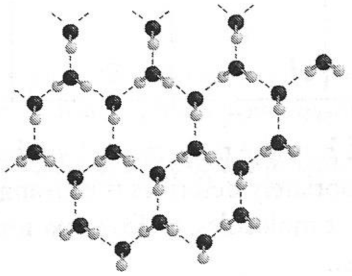
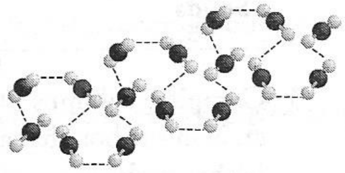
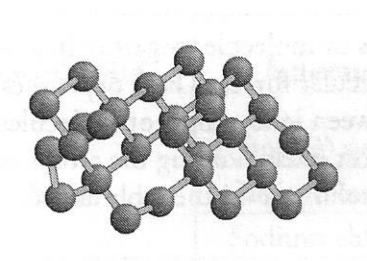
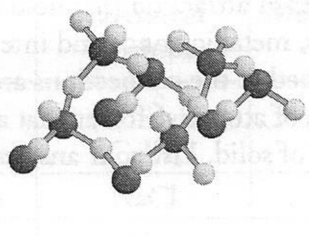
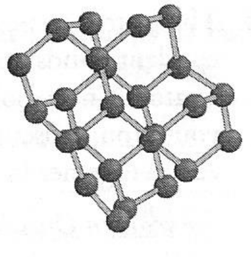
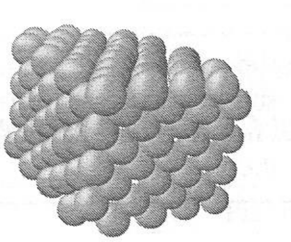
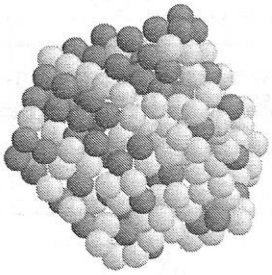
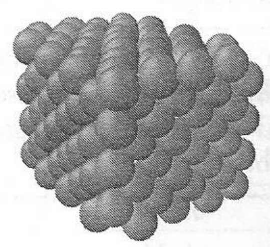
Types of Solids

What are some common categories of solids, and their properties?

Why?

Not all solids are the same. Solid substances have a tremendously wide range of melting points. Helium melts at −272 °C while tantalum hafnium carbide melts at 4215 °C. Some are conductive, others are not. Some readily dissolve in water, others do not. In this activity, you'll look at four types of solids, the types of substances that are typically in each category, and some of the properties typical for each.

Model 1 – Arrangements of Atoms in Solids

Ionic Solids	 Iron(II) Sulfide (FeS)	 Calcium Bromide ($CaBr_2$)	 Sodium Chloride (NaCl)
Molecular Solids	 Nitrogen (N_2)	 Ice (H_2O)	 Dry Ice (CO_2)
Network Covalent Solids	 Diamond (Carbon)	 Silica (SiO_2)	 Silicon (Si)
Metallic Solids	 Platinum (Pt)	 Brass (Cu and Zn)	 Nickel (Ni)

1. List the four types of solids illustrated in Model 1.

   Ionic, molecular, network covalent and metallic.

2. Complete columns A–C in the table below by referring to the examples in Model 1. Place a check in the box that appropriately describes the types of atoms that are usually seen in each type of solid.

	A	B	C	D	E	F
	All atoms are nonmetals	**All atoms are metals**	**Atoms are metals and nonmetals**	**Molecular structure**	**Formula units**	**Attractive forces**
Ionic Solids			*X*		*X*	*Ionic bonds*
Molecular Solids	*X*			*X*		*Covalent bonds* *Intermolecular forces*
Network Covalent Solids			*X*		*X*	*Covalent bonds*
Metallic Solids		*X*			*X*	*Metallic bonds*

3. Complete columns D and E in the table above by referring to the examples in Model 1. Place an X in the box that appropriately describes the arrangement of atoms or molecules in the solid (either **molecular**—distinct molecules, or **formula units**—repeating units in three dimensions with no distinct molecules).

   See table in Question 2.

4. There are four possible forces of attraction that hold atoms or molecules together in a solid: covalent bonds, ionic bonds, metallic bonds and intermolecular forces. These depend on the type of atoms in the solid and whether the connections are between ions, atoms or molecules. Within your group, discuss the type of attractive forces that are most likely holding the atoms or molecules together in each type of solid. List your answers in column F in the table above.

   See table in Question 2.

STOP

Read This!

When a solid substance is heated, the weakest attractive forces in the solid structure are overcome, and the solid melts. In some cases, this results in individual atoms or ions, and in other cases, this results in individual molecules. Regardless, melting is a physical change and does not alter the chemical formula of the substance.

5. For each type of solid in Model 1, indicate the type of attractive forces that are broken upon melting, and describe the individual particles that make up the resulting liquid.

	Bonds/forces broken upon melting	Individual particles in the liquid
Ionic	*Ionic bonds*	*Ions*
Molecular	*Intermolecular forces*	*Molecules*
Network covalent	*Covalent bonds*	*Atoms*
Metallic	*Metallic bonds*	*Atoms*

6. Match the following descriptions with one of the four types of solids.

Metallic	Metallic atoms with very loose electrons for a lattice of nuclei held together by a sea of electrons, or metallic bonds.
Molecular	Nonmetal atoms form molecules with covalent bonds. The molecules are held together in a solid by intermolecular forces of attraction.
Ionic	Metal and nonmetal atoms form a lattice of alternating positive and negative ions held together by ionic bonds.
Network covalent	Nonmetal atoms form a lattice structure held together with covalent bonds.

7. If a particular solid had very strong attractive forces, would you expect the melting point of that solid to be relatively high or relatively low? Explain your reasoning.

The melting point would be higher because the strong bonds would require more energy (higher temp) to break the solid into a liquid.

Model 2 – Melting Points and Enthalpies of Fusion

Type of Solid	Substance	Chemical Formula	Melting Point (°C)	Enthalpy of Fusion (kJ/mole)
Ionic	Iron(II) sulfide	FeS	1195	51.0
	Calcium bromide	$CaBr_2$	730	17.5
	Sodium chloride	NaCl	804	30.3
Molecular	Nitrogen	N_2	−210	0.72
	Water	H_2O	0.0	6.02
	Carbon dioxide	CO_2	−78	8.10
Network covalent	Diamond	C	3550	117.0
	Silica	SiO_2	1650	12.5
	Silicon	Si	1687	50.0
Metallic	Platinum	Pt	1770	24.0
	Brass	Cu and Zn	~930	Varies
	Nickel	Ni	1453	71.0

8. Notice that the substances listed in Model 2 are the same as those in Model 1.

   a. Which type of solid has the lowest melting points?

   Molecular solids have the lowest melting points.

   b. Is your answer in part *a* consistent with your answer to Question 7?

   Yes.

9. The **enthalpy of fusion** given in Model 2 for each substance is a measure of the energy (in kJ) needed to melt a mole of that substance.

   a. Which type of solid has the lowest enthalpies of fusion?

   Molecular solids have the lowest enthalpies of fusion.

   b. Is your answer in part *a* consistent with what you know to be the relative strength of the four types of attractive forces? Explain why or why not.

   Yes, when a molecular solid melts, the intermolecular forces are broken. These are the weakest forces so very little energy should be needed to melt these substances.

10. Using both melting point data and enthalpy of fusion data, rank the remaining three types of solids from weakest attractive forces to strongest attractive forces. Make sure there is consensus in your group before moving on.

    Molecular < Ionic = Metallic < Network covalent

Read This!

As you may have found in answering the previous question, there is a lot of overlap in properties among the four types of solids. For example, platinum (a metallic solid) has a higher melting point than several of the network covalent solids, but the majority of metallic solids have a much lower melting point than network covalent solids. The categories for solids are not as clear cut as we would like them to be; nevertheless, they are useful for predicting relative properties.

11. Use the concepts you have learned in this activity to predict the type of solid for each of the following substances. Anyone in your group should be able to justify your group's answers.

Substance	Chemical Formula	Melting Point (°C)	Enthalpy of Fusion (kJ/mole)	Type of Solid
Chlorine	Cl_2	−102	6.41	*Molecular*
Hydrogen bromide	HBr	−87	2.41	*Molecular*
Titanium	Ti	1668	20.9	*Metallic*
Sodium bromide	NaBr	747	26.1	*Ionic*
Boron	B	2076	50.2	*Network covalent*
Mercury	Hg	−38.3	2.29	*Metallic*

Read This!

Properties other than melting point and enthalpy of fusion can be helpful when categorizing a substance as one of the four types of solids. For example, conductivity and solubility can give great insight into the structure of a solid. For a substance to be soluble in water it must be charged or polar. (Remember the rule "like dissolves like.") For a substance to be conductive, in any state, there must be charged particles in a mobile state so that they can complete a circuit.

Model 3 – Solubility and Conductivity of Solids

Substance	**Chemical Formula**	**Solubility in Water**	**Conductive as a Solid**	**Conductive as a Liquid**	**Conductive in Aqueous Solution**
Iron(II) sulfide	FeS	Insoluble	No	Yes	N/A
Calcium bromide	$CaBr_2$	Very soluble	No	Yes	Yes
Sodium chloride	$NaCl$	Very soluble	No	Yes	Yes
Nitrogen	N_2	Slightly soluble	No	No	No
Water	H_2O	N/A	No	Slightly	N/A
Carbon dioxide	CO_2	Slightly soluble	No	No	No
Diamond	C	Insoluble	No	No	N/A
Silica	SiO_2	Insoluble	No	No	N/A
Platinum	Pt	Insoluble	Yes	Yes	N/A
Brass	Cu and Zn	Insoluble	Yes	Yes	N/A
Nickel	Ni	Insoluble	Yes	Yes	N/A

N/A = not applicable

12. Refer to Model 3.

    a. Which type(s) of solid is generally very soluble in water?

    Ionic substances are most soluble in water.

    b. Which type(s) of solid is least soluble in water?

    Metallic and network covalent substances are least soluble in water.

13. Refer to Model 3.

    a. Which type of solid is most conductive in the solid state?

    Metallic substances are most conductive as solids.

    b. Use the concepts you have learned about the type of solid in part *a* to explain why it is conductive in the solid state.

    Metals contain very mobile valence electrons that can move in the solid to conduct an electric current.

14. Explain why ionic substances would be conductive after they are melted, even though they are not conductive as solids.

    As solids, the ions in an ionic solid are stuck in a crystal lattice—they are not mobile. Once the solid is melted however, the ions become mobile and can move in the liquid state to conduct an electric current.

Extension Questions

15. The last column in Model 3 (Conductive in Aqueous Solutions) has several N/A entries. Give two reasons why conductivity data for those substances would not exist.

    If the substance is insoluble, it would be impossible to measure conductivity data for an aqueous solution.

16. Engineers use materials to perform different functions based on the properties of the materials. For centuries we have used metals for tools and more recently for electrical circuits. What properties of metallic solids make them well suited for this purpose?

    Metals are strong, insoluble and conductive as a solid. You would not want your electrical circuits to break easily, dissolve on a rainy day or be resistant to electrical current.

Teacher Resources – Types of Solids

Learning Objectives

1. Describe four types of solids (metallic, ionic, molecular and network covalent) based on the types of bonds that hold the solid together.
2. Predict the relative melting point and enthalpy of fusion for two substances based on the type of solid they form.
3. Use the chemical formula, melting point and heat of fusion data to determine the type of solid the substance forms.

Prerequisites

1. Students should have working knowledge of covalent, ionic and metallic bonding and intermolecular forces, including the relative strengths of these attractive forces and the types of substances that typically have these bonds.
2. Students should be familiar with the enthalpy of fusion of a solid.
3. Students should be able to explain why some substances (including solutions) conduct electricity.

Assessment Questions

1. Which statement below correctly describes network covalent bonding, in most cases?
   a. Atoms of one or more nonmetal elements bonded with covalent bonds into molecules that are weakly held by intermolecular forces.
   b. Atoms of metal and nonmetal elements bonded with covalent bonds in a lattice structure.
   c. Atoms of one or more nonmetal elements bonded with covalent bonds in a lattice structure.
   d. Atoms of one or more metals bonded with covalent bonds in a lattice structure.
2. Molecular solids tend to have
   a. high melting points and high enthalpies of fusion.
   b. low melting points and high enthalpies of fusion.
   c. high melting points and low enthalpies of fusion.
   d. low melting points and low enthalpies of fusion.
3. Stannic chloride ($SnCl_4$) has a melting point of −33 °C and is not conductive as a liquid. What type of solid does stannic chloride form? Support your answer with a full explanation.

Assessment Target Responses

1. *c*
2. *d*
3. *By simply looking at the chemical formula of stannic chloride, one would be tempted to say that it is an ionic compound because it contains metal and nonmetal atoms. However, the properties stated are*

not consistent with this answer. If it were an ionic compound, it would have a very high melting point and be conductive in its liquid state. Likewise, it cannot be a network covalent solid because of its low melting point. Because the nonmetal is present, and it is nonconductive in its liquid state, it cannot be a metallic solid. That leaves molecular as the only option left. Although this is unusual for a compound made from a metal and nonmetal, the properties it exhibits are consistent with this type of solid structure.

Teacher Tips

- Students often want the "rules" of chemistry to be unambiguous, but unfortunately the properties involved with different types of solids do not follow the rules all the time. This provides a good opportunity to discuss the difference between "trends" and "scientific laws."
- One category of substances that is not addressed in this activity is ternary ionic compounds (e.g. $NaNO_3$ or $CuSO_4$). It may be helpful to show models or simulations of these ionic solids to show students that the general structure of these compounds is similar to binary ionic compounds but with covalently-bonded polyatomic ions replacing some of the lattice points.
- Brass was intentionally used as an example in Model 1 to illustrate that an alloy has metallic bonding similar to pure metals. In Model 2 however, the properties of brass cannot be defined specifically because both the melting point and enthalpy of fusion would depend on the particular ratio of the copper and zinc in the brass.
- Students are able to visualize the three-dimensional structure of these solids much better with physical models. In the Crystal Structure—Super Value Laboratory Kit available from Flinn Scientific (Catalog No. AP7036), students build models of cubic crystal lattice structures and then analyze the models to determine the number of atoms or ions in each unit cell.

Alignment with the AP Chemistry Framework

- **Essential Knowledge 2.A.1:** The different properties of solids and liquids can be explained by differences in their structures, both at the particulate level and in their supramolecular structures.

  Learning Objective 2.3 The student is able to use aspects of particulate models (i.e., particle spacing, motion, and forces of attraction) to reason about observed differences between solid and liquid phases and among solid and liquid materials.

- **Essential Knowledge 2.D.1:** Ionic solids have high melting points, are brittle, and conduct electricity only when molten or in solution.

  Learning Objective 2.24 The student is able to explain a representation that connects properties of an ionic solid to its structural attributes and to the interactions present at the atomic level.

- **Essential Knowledge 2.D.2:** Metallic solids are good conductors of heat and electricity, have a wide range of melting points and are shiny, malleable, ductile and readily alloyed.

  Learning Objective 2.26 Students can use the electron sea model of metallic bonding to predict or make claims about the macroscopic properties of metals or alloys.

  Learning Objective 2.28 The student is able to explain a representation that connects properties of a metallic solid to its structural attributes and to the interactions present at the atomic level.

- **Essential Knowledge 2.D.3:** Covalent network solids generally have extremely high melting points, are hard, and are thermal insulators. Some conduct electricity.

  Learning Objective 2.30 The student is able to explain a representation that connects properties of a covalent solid to its structural attributes and to the interactions present at the atomic level.

- **Essential Knowledge 2.D.4:** Molecular solids with low molecular weight usually have low melting points and are not expected to conduct electricity as solids, in solution, or when molten.

  Learning Objective 2.32 The student is able to explain a representation that connects properties of a molecular solid to its structural attributes and to the interactions present at the atomic level.

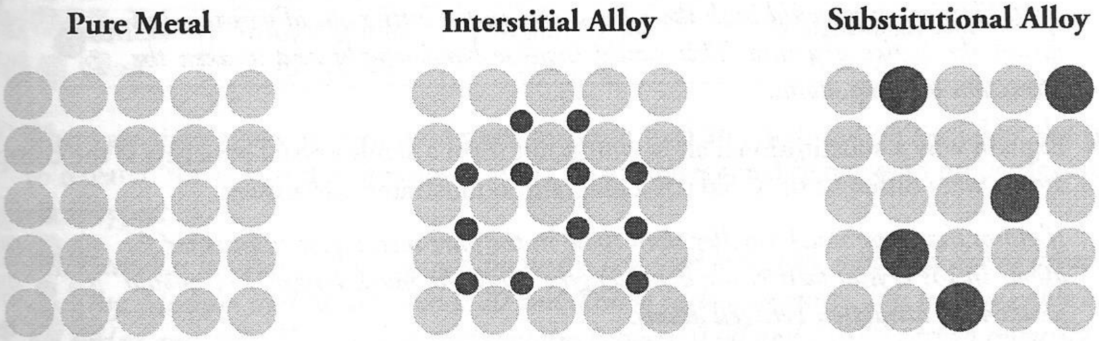
Alloys

How are alloys made and what properties do they have?

Why?

Metals are amazing, and they are all around us. You can probably easily identify them by their shiny surfaces and tinny sound when you tap them. We use metals to run electricity through our house, manufacture our cars, and create circuits for our phones. However, most metals in their pure form are less than perfect for these jobs. Luckily, the properties of metals can be manipulated to make them more useful by adding other elements to form a mixture. These mixtures are called **alloys**. In this activity, you will look at two types of alloys and their properties.

Model 1 – Two Types of Alloys



Pure Metal **Interstitial Alloy** **Substitutional Alloy**

1. Name the two types of alloys illustrated in Model 1.

   Substitutional and interstitial.

2. According to Model 1, how is an alloy different from a pure metal?

   An alloy contains more than one type of metal atom.

3. Consider the two types of alloys in Model 1. Based on the diagrams and your understanding of English words, define "substitutional" and "interstitial."

   In substitutional alloys, an atom of the impurity replaces an atom in the original crystal lattice. In this case, "impurity" does not mean unwanted. Rather, it is referring to atoms not in the original crystal lattice. "Impurity" atoms can be thought of as the minority component in the alloy, which is a solid solution.

   In interstitial alloys, atoms of the impurity are added in the spaces between the atoms of the original crystal lattice.

4. One of the alloys in Model 1 tends to form when elements with similar sized atoms are melted together and allowed to cool. The other type forms when elements with very different sized atoms are combined. Match the descriptions below with each type of alloy.

Component atoms are similar size.	*Substitutional alloys.*
Component atoms are different sizes.	*Interstitial alloys.*

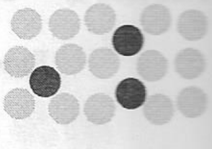
Read This!

It is possible to mix two metal elements together and simply form a mixture of metals that would not be considered an alloy. The distinction is in the properties that result from the mixture. If the addition of an "impurity" to the metal somehow causes a change in a property that is beneficial, then the mixture is considered an alloy. If however the "impurity" results in weakening the metal or causes less desirable properties, then it is considered simply a mixture.

5. Solids are most stable when the arrangement of atoms in the crystal lattice minimizes bond length, maximizes bond strength, and maximizes the number of atoms "touching" one another—in other words, when the atoms fill the space most efficiently.

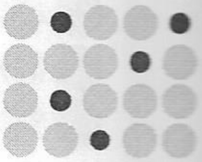
   a. Explain why an interstitial alloy would not form a stable crystal structure if the component atoms were of similar size. Sketch a diagram to illustrate your answer.

   If atoms of similar size tried to fit in the interstitial spaces between atoms in the crystal lattice, they would push the other atoms in the lattice out of position and distort the lattice structure. This would increase bond lengths and weaken the attraction between atoms.



   b. Explain why a substitutional alloy would not form a stable crystal structure if the component atoms were different sizes. Sketch a diagram to illustrate your answer.

   If atoms that were much smaller than those in the pure metal were substituted for atoms in the crystal lattice, the bond lengths would be much longer. This would weaken the attraction between atoms.



6. Consider how the density of an alloy might compare to the density of the original metals.

   a. Would substitutional alloys tend to have a density similar to, significantly greater than or significantly less than the pure metal? Explain your reasoning.

   Substitutional alloys would tend to have a density similar to the pure metal because the atoms that are being added are of similar size (and it could be assumed similar mass). They are taking the place of an atom that was already present in the crystal lattice. Therefore, there is very little change to the mass and no change to the volume of the metal.

   b. Interstitial alloys oftentimes have a density less than the pure metal. Explain how the addition of a small, low mass atom like carbon could make the density of an interstitial alloy less than the pure metal.

   If the small interstitial atoms slightly spread the crystal lattice when they were added, the total volume of the alloy would increase. This could lower the density regardless of the added mass from the interstitial atoms.

7. Metals are malleable because of weak bonds between atoms. This allows planes of atoms to slide past one another and into new positions. Some alloys retain their malleability while others become more rigid. Consider the diagrams in Model 1. Predict which type of alloy would result in a more rigid substance. Justify your reasoning.

   The interstitial alloy would be more rigid than the pure metal because the atoms in the interstitial spaces of the crystal lattice will hinder the movement of planes of atoms when the metal is bent.

Extension Questions

8. Listed below are the components of several common alloys used in industry today. Use a reference table of atomic radii to determine if the alloy is likely to be interstitial or substitutional based on what you learned from Model 1.

Alloy	Components	Atomic Radii	Type of Alloy Structure
Brass	Copper, Zinc	*145 pm, 142 pm*	*Substitutional*
Bronze	Copper, Tin	*145 pm, 145 pm*	*Substitutional*
Steel	Iron, Carbon	*156 pm, 67 pm*	*Interstitial*
Pewter	Lead, Antimony, Bismuth, Silver	*154 pm, 133 pm, 143 pm, 165 pm*	*Substitutional*
Stainless Steel	Iron, Carbon, Chromium	*156 pm, 67 pm 166 pm*	*Substitutional and Interstitial*

9. There are three types of steel; mild steel, medium steel and high carbon steel. Use the Internet to research the uses and properties of steel. What causes the differences in properties among the three types?

Mild steel has less than 0.20% carbon impurity. It is used for cables, nails and chains because of its ductility. Medium steel has between 0.20 and 0.60% carbon impurity. It is less malleable and is used for girders and rails. High carbon steel contains between 0.60 and 1.50% carbon impurity. It is the least malleable and is used for tools, cutlery and springs.

Teacher Resources – Alloys

Learning Objectives

1. Identify an alloy as substitutional or interstitial when given a drawing of the crystal lattice structure.
2. Predict changes in properties such as density and malleability to a metal when an alloy of either type is formed.

Prerequisites

1. Students should have an understanding of metallic bonding and how the "sea of electrons" results in metallic properties.
2. Students should understand that the strength of attractive forces in a bond is affected by distance between the atoms.
3. Students should have a good understanding of density.

Assessment Questions

1. The density of an interstitial alloy will be
   a. similar to the density of the pure metal.
   b. less than the density of the pure metal.
   c. greater than the density of the pure metal.
   d. difficult to predict without measurements.
2. What is the difference between a mixture of metals and an alloy?
3. If two metallic elements of similar size were melted and mixed together, what type of alloy would you expect to form, substitutional or interstitial?

Assessment Target Responses

1. *b*
2. *For a mixture of metals to be considered an alloy, there must be some desirable property that results from the addition of the impurity.*
3. *Substitutional.*

Alignment with AP Chemistry Framework

- **Essential Knowledge 2.D.2:** Metallic solids are good conductors of heat and electricity, have a wide range of melting points, and are shiny, malleable, ductile and readily alloyed.

  Learning Objective 2.25 The student is able to compare the properties of metal alloys with their constituent elements to determine if an alloy has formed, identify the type of alloy formed, and explain the differences in properties using particulate level reasoning.

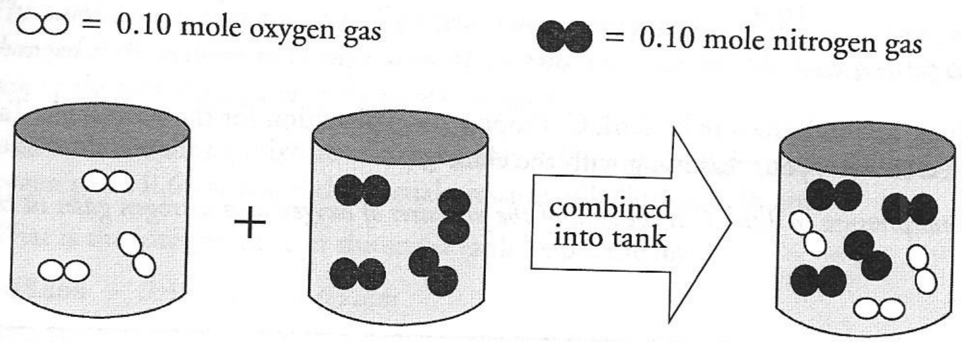
Partial Pressures of Gases

How do mixtures of gases affect the overall pressure?

Why?

It would be nice if chemists only worked with pure samples of gas. However, there is an ever present gas mixture that chemists must consider in all situations—air. When we use air as a source of oxygen for chemical reactions, we must be able to calculate the moles, volume and pressure of the oxygen in that mixture. In this activity, you will learn how to mathematically calculate the pressure of a gas that is present in a mixture of other gases.

Model 1 – A Mixture of Gases



	Tank A	Tank B	Tank C
Volume	10.00 L	10.00 L	10.00 L
Temperature (K)	298 K	298 K	298 K
Moles O_2 gas	*0.30 mole*	*0*	*0.30 mole*
Moles N_2 gas	*0*	*0.40 mole*	*0.40 mole*
Pressure O_2 (atm)	*0.74 atm*	*0*	*0.74 atm*
Pressure N_2 (atm)	*0*	*0.98 atm*	*0.98 atm*
Total Pressure	*0.74 atm*	*0.98 atm*	*1.71 atm*

1. Consider Model 1. What do all three tanks have in common?

   All tanks have a volume of 10.0 L. All tanks have a temperature of 298 K. All tanks are the same shape.

2. Determine the moles of oxygen gas and the moles of nitrogen gas for each tank in Model 1 and enter those values in the table.

   See Model 1.

3. Use the Ideal Gas Law to calculate the pressure of the oxygen gas in Tank A. Enter that value in the Model 1 table.

$$P = \frac{0.30\,mole\left(0.08206\,\frac{atm\cdot L}{mole\cdot K}\right)(298\,K)}{10.0\,L}$$

$P = 0.74\ atm$

4. Use the Ideal Gas Law to calculate the pressure of the nitrogen gas in Tank B. Enter that value in the Model 1 table.

$$P = \frac{0.40\,mole\left(0.08206\,\frac{atm\cdot L}{mole\cdot K}\right)(298\,K)}{10.0\,L} \qquad P = 0.98\ atm$$

$P = 0.98\ atm$

5. Consider the total pressure in Tank C. Propose an explanation for the pressure in Tank C and be prepared to share your reasoning with the class.

The total pressure in Tank C is the sum of the pressures of oxygen and nitrogen gases in the tank.

Read This!

Consider a single oxygen gas molecule in Tank C of Model 1. From its perspective nothing changed when it moved from Tank A to Tank C. The volume available to move in is still 10.00 L. The temperature is still 298 K. It will still hit the sides of the tank just as often and just as hard as it did before it was combined with the nitrogen gas sample, assuming gas molecules are very small. Therefore, the pressure that the group of oxygen molecules exerts in Tank C is the same as the pressure that they exerted in Tank A. However, in Tank C we call the pressure that the oxygen molecules exert against the container walls a **partial pressure** because it is not the only gas contributing to the total pressure of the gas mixture in the tank.

6. Enter the partial pressure values for oxygen gas and nitrogen gas in Tank C of Model 1.

See Model 1.

7. Write a mathematical equation to show the relationship between the partial pressures of oxygen gas (P_{O_2}) and nitrogen gas (P_{N_2}) and the total pressure (P_T).

$P_T = P_{O_2} + P_{N_2}$

8. With your group, write a statement describing how combining the gases at constant temperature and volume affected the pressure of each gas.

When gases are combined at constant temperature and volume, they retain their original pressure in the new container as a partial pressure.

Read This!

Dalton's Law of Partial Pressures states that the total pressure exerted by an ideal gaseous mixture is equal to the sum of the partial pressures of each individual component in the mixture.

$$P_T = P_1 + P_2 + P_3 \ldots \text{or } P_T = \sum P_i$$

9. A chemistry student uses a pressurized tank to add 0.20 atm of a third gas, Gas Z, to tank C in Model 1.

   a. What is the partial pressure of the component gases after the addition of Gas Z?

   $P_{O_2} = 0.73\,atm$ $\quad$ $P_{N_2} = 0.98\,atm$ $\quad$ $P_Z = 0.20\,atm$

   b. What is the total pressure in the tank with all three gases present? Show your work.

   $0.73\,atm + 0.98\,atm + 0.20\,atm = 1.91\,atm$

   c. A chemistry student performs a reaction in the tank which consumes all of the oxygen gas. Assuming the temperature and volume of the tank remain constant, determine the partial pressures of the remaining gases as well as the total pressure in the tank. Explain your answer.

   $P_{O_2} = 0\,atm$ $\quad$ $P_{N_2} = 0.98\,atm$ $\quad$ $P_Z = 0.20\,atm$ $\quad$ $P_{total} = 1.18\,atm$

   The partial pressure of oxygen will be zero. The partial pressures of the remaining gases will be unchanged if the volume and temperature of the tank are constant. The total pressure is equal to the sum of the partial pressures of the unreacted gases.

10. A scuba tank contains a mixture of oxygen and helium gases. Before the dive, the partial pressure of oxygen gas is 0.65 atm and the partial pressure of helium is 0.38 atm.

    a. What is the total pressure in the scuba tank before the dive?

    $0.65\,atm + 0.38\,atm = 1.03\,atm$

    b. After the dive, the partial pressure due to the oxygen gas is reduced by 80%. Calculate the final partial pressure of oxygen in the tank.

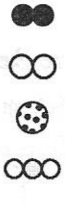
    $0.20(0.65\,atm) = 0.13\,atm$ *final pressure of* O_2

    c. If the total pressure in the scuba tank after the dive is 0.21 atm, what is the partial pressure of the helium gas? Show your work.

    $0.21\,atm - 0.13\,atm = 0.08\,atm$ *final pressure of He*

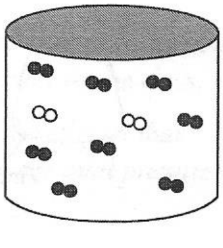
Model 2 – Air

Composition of Dry Air	
Nitrogen	78.084%
Oxygen	20.948%
Argon	0.934%
Carbon Dioxide	0.035%



11. Consider the information provided in Model 2. Discuss with your group how you might illustrate air as a mixture of molecules in the tank in Model 2. Draw a particulate illustration of air.

    Groups may come up with a variety of correct illustrations. Some may draw 10 molecules, others may draw 100 molecules. They must however accurately approximate the relative amounts of gasses in the tank based on the data given. Discuss the pros and cons of the different illustrations among the class. For example, using 10 molecules precludes inclusion of carbon dioxide in the illustration owing to its small percent composition of the mixture.



12. On a particular day, the air pressure in the chemistry lab is 1.137 atm. Discuss with your group how you might perform the following calculations, and then do them. Show your work so that you can refer back to these calculations later.

   a. What is the partial pressure of oxygen in the room on that day?

   $1.137\ atm\ (0.20947) = 0.2382\ atm$

   b. How many moles of oxygen molecules would be in a 10.0-L sample of air from the room on that day (assume room temperature is 22 °C)? Show your work.

$$n = \frac{PV}{RT} = \frac{0.2382\ atm\,(10.0\ L)}{\left(0.08206\ \frac{atm \cdot L}{mole \cdot K}\right)(295\ K)} = 0.984\ mole$$

13. A student wants to burn a 1.00-g sample of ethanol (C_2H_5OH) in a jar containing air. Assuming the air in the jar is at standard atmospheric pressure and room temperature (22 °C), what volume will the jar need to be in order to hold enough oxygen for complete combustion?

   a. Write a balanced chemical reaction for the combustion of ethanol.

   $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

   b. Calculate the moles of oxygen needed to completely combust the ethanol.

$$1.00\ g\ ethanol\left(\frac{1\ mole}{46.0688\ g}\right)\left(\frac{3O_2}{C_2H_5OH}\right) = 0.0651\ mole\ O_2\ needed$$

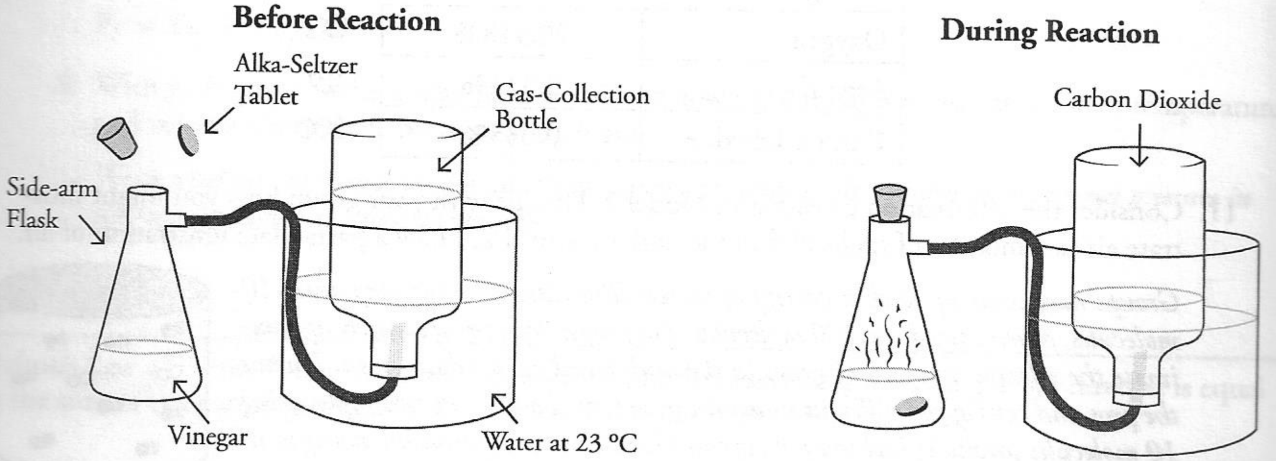
   c. Calculate the partial pressure of oxygen in the jar.

   $1.00\ atm\ (0.20974) = 0.20974\ atm$

   d. Calculate the volume of oxygen needed in the jar.

$$V = \frac{nRT}{P_{O_2}} = \frac{(0.0651\ mole)\left(0.08206\ \frac{atm \cdot L}{mole \cdot K}\right)(295\ K)}{0.20974\ atm} = 7.51\ L$$

Model 3 – Collecting Gases over Water



14. According to Model 3, what gas is being produced by the reaction in the side-arm flask?

Carbon dioxide.

15. Describe how the gas is being collected as it is produced in Model 3.

As gas is produced by the reaction, it travels through the tube and is released into the gas collection bottle. The gas pushes the water out of the bottle, lowering the water level inside the bottle and trapping the gas.

16. Assuming the gas-collecting bottle was initially completely filled with water, what gas(es) are present in the bottle after the reaction? *Hint:* Consider what gas is always present when liquid water is present.

Carbon dioxide and water vapor are in the gas-collecting bottle.

17. Considering your answer to Question 16, write a mathematical equation to show how the total pressure inside the bottle might be calculated using partial gas pressures.

$$\mathrm{P}_{CO_2} + \mathrm{P}_{H_2O} = P_T$$

18. The vapor pressure of water is well known, and dependent only on the temperature of the liquid water sample.

Water temperature (°C)	Vapor pressure (mmHg)
20	17.5
21	18.7
22	19.8
23	21.1
24	22.4

a. Use the table above to determine the vapor pressure (and therefore the partial pressure) of water in the gas-collecting bottle in Model 3. Convert the value to atmospheres.

The vapor pressure of water at 23 °C is 21.1 mmHg.

$$21.1\,mmHg\left(\frac{1\,atm}{760\,mmHg}\right) = 0.0278\,atm$$

b. If the atmospheric pressure in the lab and in the bottle is 0.989 atm, what is the partial pressure of the gas collected?

$$0.989\,atm - 0.0278\,atm = 0.961\,atm$$

c. How many moles of gas would be collected if the volume of the bottle is 1.00 L? (Assume the liquid water that was originally in the bottle has been completely pushed out by gas.)

$$\mathrm{n} = \frac{\mathrm{PV}}{\mathrm{RT}} = \frac{0.961\,atm\,(1.00\,L)}{\left(0.08206\,\frac{atm \cdot L}{mole \cdot K}\right)(296\,K)} = 0.0396\,mole$$

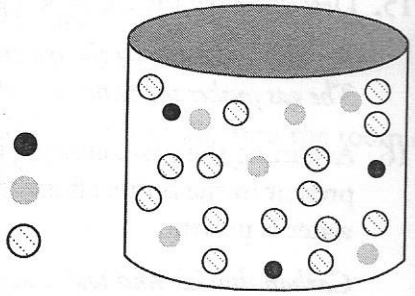
19. Would Dalton's law hold true if two of the gases in the mixture reacted with each other to form a gaseous product? Discuss this in your group and be prepared to justify your answer to the class.

This would only hold true if the moles of gaseous product equaled the sum of the moles of gases that reacted. If the total moles of gas either increased or decreased because of the reaction, the total pressure would not equal the sum of the partial pressures before the reaction.

Extension Questions

Model 4 – Mole Fraction

Gas	Partial Pressure, P_i	Moles	Mole Fraction, X_i
Helium	0.35 atm	0.100	0.125
Argon	0.70 atm	0.200	0.250
Krypton	1.75 atm	0.500	0.625



20. Consider the tank of gas illustrated in Model 4. What is the total pressure in the tank?

    $0.35\,atm + 0.70\,atm + 1.75\,atm = 2.80\,atm$

21. According to Model 4, what is the symbol for mole fraction?

    The symbol for mole fraction is X_i.

22. Use the data in Model 4 to derive a mathematical equation for mole fraction. Brainstorm possible equations with your group and divide the work to check each idea. When you think you have the correct equation, check to see that it can be used to successfully calculate all three mole fractions in the table in Model 4.

    $$X_i = \frac{\textit{moles of gas i}}{\textit{total moles in the mixture}}$$

    For example: $X_{He} = \dfrac{0.100\,mole}{0.100\,mole + 0.200\,mole + 0.500\,mole} = \dfrac{0.100\,mole}{0.800\,mole} = 0.125$

23. The mole fraction of a gas, X_i, can be used with the total pressure of the gas mixture, P_T, to calculate the partial pressure of the gas, P_i. Derive a mathematical equation for this relationship and check to see that it works using your answer in Question 20 and the data in Model 4.

    $P_i = X_i \cdot P_T$

    For example: $P_{He} = 0.125\,(2.80\,atm) = 0.35\,atm$

Teacher Resources – Partial Pressures of Gases

Learning Objectives

1. Use Dalton's law of partial pressure to find the total pressure of a mixture of gases given the partial pressures.
2. Calculate the partial pressures of gases given the percent composition of a gaseous mixture.
3. Use partial pressures in Ideal Gas Law calculations to find volumes or moles of gases.

Prerequisites

1. Students should be comfortable with the calculation of volume, pressure or moles of a gas using the Ideal Gas Law.
2. Students should understand that the pressure exerted by a gas is independent of the identity of the gas. It is only a function of the moles, volume and temperature (kinetic energy) of the gas sample.
3. Students should be able to calculate the moles and volumes of gaseous reactants or products needed for a chemical reaction.

Assessment Questions

1. Dalton's law of partial pressures states:
   - *a.* The total pressure of a mixture of gases is equal to the product of the partial pressures of each component gas.
   - *b.* The total pressure of a mixture of gases is equal to the sum of the partial pressures of each component gas.
   - *c.* The total pressure of a mixture of gases is equal to the difference in the partial pressures of each component gas.
   - *d.* The total volume of a mixture of gases is equal to the sum of the partial volumes of each component gas.
2. Three gases are mixed in a 1.00-L vessel. The total pressure of the gas mixture is 845 mmHg. If the partial pressure of gas A is 623 mmHg and the partial pressure of gas B is 100 mmHg, what is the partial pressure of gas C?
3. What is the partial pressure of nitrogen in air on a day when the atmospheric pressure is 1.08 atm?

Assessment Questions Target Responses

1. *b.*
2. $845\,mmHg - 623\,mmHg - 100\,mmHg = 122\,mmHg$
3. $1.08\,atm\,(X_{N_2}) = P_{N_2}$

$$X_{N_2} = \frac{2.786}{2.786 + 0.688} = 0.80 \qquad P_{N_2} = 1.08 \times 0.80 = 0.866\,atm$$

Teacher Tip

- Supplement the unit on gas laws with dynamic, interactive computer models available online, such as at http://intro.chem.okstate.edu.

Alignment with the AP Chemistry Framework

- **Essential Knowledge 2.A.2:** The gaseous state can be effectively modeled with a mathematical equation relating various macroscopic properties. A gas has neither a definite volume nor a definite shape; because the effects of attractive forces are minimal, we usually assume that the particles move independently.

  Learning Objective 2.6 The student can apply mathematical relationships or estimation to determine macroscopic variables for ideal gases.

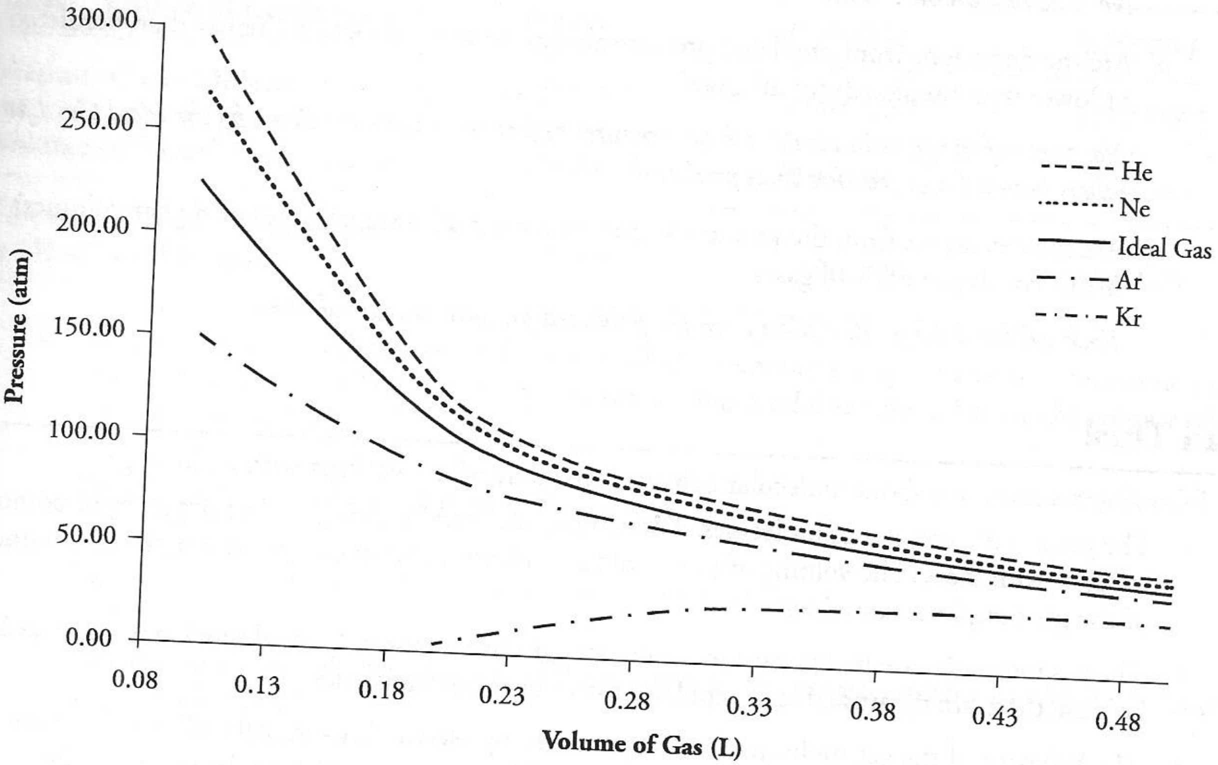
Deviations from the Ideal Gas Law

Does the Ideal Gas Law accurately calculate the pressure of a gas?

Why?

The equation $PV = nRT$, otherwise known as the Ideal Gas Law, is a powerful tool. A scientist can predict the pressure, volume, number of moles or temperature of a gas when the other variables are measurable. But how accurate is the calculated value? In real life we deal with real gases, not ideal gases. Can one simple equation predict all of these variables for all gases? Or does it only approximate the real values? What factors determine how well the Ideal Gas Law equation can predict values for real gases?

Model 1 – Deviations from Ideal



1. Consider the data in Model 1 for several gases measured at constant temperature.
   a. The relationship between what two gas variables is shown in the graph?

      The graph shows the relationship between the pressure of the gas and the volume of the gas.

   b. Which line shows the predicted relationship between those two variables?

      The Ideal Gas line shows the predicted relationship between pressure and volume.

   c. The Ideal Gas Law, $PV = nRT$, shows the mathematical relationship between all gas variables. *Rearrange the variables above to write the equation for the line that gives the predicted relationship between the two variables in the graph above.*

      $$P = (nRT)\frac{1}{V}$$

2. The relationships between pressure and volume of four real gases are shown in Model 1. What four gases are illustrated?

   Helium, neon, argon and krypton gases are shown in the graph in Model 1.

3. Of the four real gases included in Model 1, which has the largest deviations from the predicted pressure?

   Krypton has the largest deviations from the predicted pressure in Model 1.

4. Discuss as a group how the actual pressures of the four gases deviate from that predicted by the Ideal Gas Law. Be sure to consider the following questions.

   a. Do all real gases have the same deviation from the predicted pressure?

   No. The real pressure–volume curve for each real gas is very different.

   b. Are the deviations from predicted pressure always the same direction (higher than predicted or lower than predicted) for all gases?

   No. Some of the gases in Model 1 have pressures higher than those predicted by the Ideal Gas Law, others have a lower pressure than predicted.

   c. Are the deviations from the predicted pressure greater at lower volumes or higher volumes? Is this consistent with all gases?

   Each gas has a larger deviation from the predicted pressure at low volumes.

Read This!

The following assumptions about molecular behavior are made when working with an ideal gas:

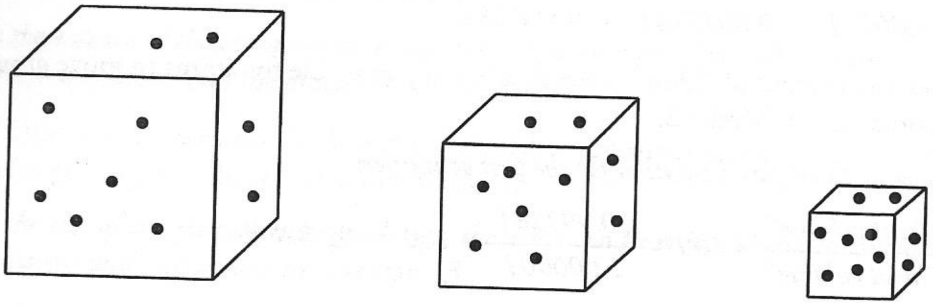
- The gas sample consists of molecules. These molecules can be thought of as single, rigid points in space with mass. The volume of these points is infinitesimal in comparison with the volume of the gas sample or container.
- The gas molecules are in constant, random, straight line motion. Curved motion is not possible because there are no attractive or repulsive forces between molecules.
- The behavior of the gas molecules can be predicted by Newton's Laws. All collisions between molecules and between molecules and the walls of the container are completely elastic. No energy is lost to friction or heat.
- The gas molecules have a distribution of speeds and kinetic energies—some move faster than others. The temperature of the gas in Kelvins is proportional to the average kinetic energy of the molecules.

5. Consider the assumptions set forth in the *Read This!* box. Discuss with your group the major inconsistencies with real gases. In other words, what statements in the *Read This!* box are less applicable when working with real gases?

   Answers will vary. Students should recognize that gas molecules do have volume, so assuming they are infinitesimal will lead to errors. Students may also question the lack of attractive or repulsive forces. In the natural motion of gas molecules within the container, it is possible that two molecules may be close enough that some attractive forces will be present.

STOP

Model 2 – Volume of Gas Molecules



Moles of Gas	1.0000 mole	1.0000 mole	1.0000 mole
"Ideal" Volume of Container	1.00000 L	0.50000 L	0.25000 L
Volume of Gas Molecules	*0.001718 L*	*0.001718 L*	*0.001718 L*
Volume of "Real" Usable Space	*0.99828 L*	*0.49828 L*	*0.24828 L*
Percent of "Ideal" Volume that is "Real" Usable Space	*99.828%*	*99.656%*	*99.312%*

6. Imagine that each of the three containers in Model 2 contains krypton atoms. The atomic radius of a krypton atom is 88.00 pm. Assuming the atom is a solid sphere, calculate the volume of one krypton atom in liters.

   Hint: Volume of a sphere equation is $V = \frac{4}{3}\pi r^3$

   $$V_{Kr} = \frac{4}{3}(3.14159)(8.800 \times 10^{-10} dm)^3 = 2.855 \times 10^{-27} L$$

7. Calculate the total volume occupied by the krypton atoms in each container in Model 2. Enter these data in the table.

   $$\left(2.855 \times 10^{-27} \frac{L}{atoms}\right)\left(6.022 \times 10^{23} \frac{atoms}{mole}\right)(1.000\,mole) = 0.001718\,L$$

Read This!

According to the assumptions of the Ideal Gas Law, atoms of gas have no volume. Therefore, if a krypton atom is in a 1.00000-L container it has, theoretically, 1.00000 L of space to roam—regardless of how many other krypton atoms are present in the container. Theoretically those other atoms do not take up space. In a real gas however, the other krypton atoms **do** take up space. Therefore, the krypton atom in question does not really have 1.00000-L of space in which to roam since it cannot be in the space occupied by another atom. So, the usable space, from that atom's perspective, is less than the volume of the container.

8. Calculate the "real" usable space in each of the containers in Model 2.

   V = $1.00000L - 0.001718L = 0.99828L$

9. Calculate the percent of "ideal" space that is really available for atoms to move around in for each of the containers in Model 2.

   See Model 2. Example calculation for the first container:

$$\% = \frac{\text{"real volume"}}{\text{"ideal volume"}} \times 100 = \frac{0.99828L}{1.00000L} \times 100 = 99.828\%$$

10. According to Model 2, as the container containing the same amount of gas gets smaller, what happens to the percent available space for atom motion?

    As the container holding the gas gets smaller, the percent of space that is available gets smaller. In other words, the gas molecules take up a greater percentage of the available space.

11. The ideal gas law equation can be used to predict the pressure of a gas in a 1.00000-L container. However, as you have just discovered, the atoms in that container do not really have 1.00000-L of space to occupy—they have less. How would this affect the observed pressure—would it be higher or lower than that predicted by the Ideal Gas Law? Explain your reasoning using the Ideal Gas Law equation.

    Since the real volume is smaller than the measured volume, the pressure would be higher. According to the Ideal Gas Law equation, pressure and volume are inversely proportional.

12. As the container holding the same amount of gas gets smaller, would the deviation between the observed pressure and predicted pressure increase or decrease? Justify your answer with information from Model 2.

    As the gas container gets smaller, the deviation would be greater because the difference between the ideal volume and real volume is larger in a small container.

13. Not all gas molecules are the same size. Predict how the deviation from ideal behavior might change as the gas molecules become larger.

    If the gas molecules are larger, then the deviation from ideal pressure would increase because more of the ideal volume would be occupied by the gas molecules. The differences between the ideal volume and the real volume would be even greater.

14. Revisit the graph in Model 1 and consider your answers to Questions 11–13. Are your answers supported by the data in Model 1? Provide specific evidence from the graph to justify your answers.

    a. In Question 11, we said the space occupied by atoms should cause the pressure to be __________ than predicted. Is this observed in Model 1?

    In Question 11, we predicted the pressure would be higher for all gases since the available volume was less than what was measured. However, in Model 1 only helium and neon have pressures higher than those predicted by the Ideal Gas Law. The other two gases have real pressures that are lower than the predicted pressure.

b. In Question 12, we said the deviation from ideal pressure should __________ as the container gets smaller. Is this observed in Model 1?

As the volume of the container decreases, the deviation from ideal behavior increases in all cases. This is consistent with the answer in Question 12.

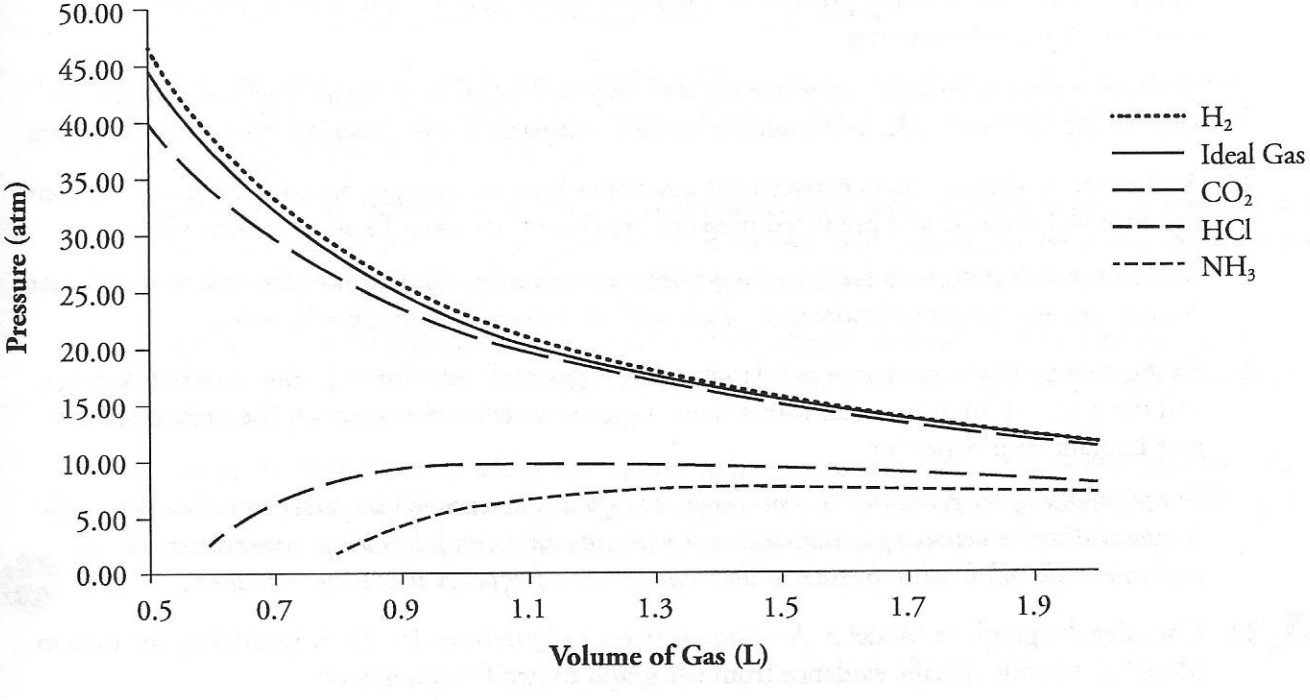
c. In Question 13, we said the deviation from ideal pressure should __________ as the gas molecules get larger. Is this observed in Model 1?

As the size of the gas molecules gets larger, the deviation from ideal behavior increases. This is consistent with the answer in Question 13.

15. Based on the information in Models 1 and 2, does the volume of gas molecules fully explain deviations from ideal gas behavior?

No, the volume of gas molecules cannot explain why some gases have pressures that are lower than the predicted pressure.

Model 3 – Polarity of Gas Molecules



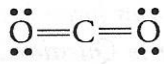
16. Which four gases are compared to ideal gas behavior in Model 3?

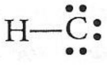
Hydrogen, carbon dioxide, hydrogen chloride and ammonia are shown in Model 3.

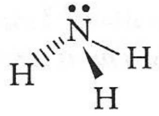
17. Of the four gases in Model 3, which are polar and which are nonpolar? Draw dot diagrams to support your answer.

Hydrogen and carbon dioxide are considered nonpolar. Hydrogen chloride and ammonia would be polar.

H—H







18. Based on the data in Model 3, does polarity seem to affect the deviation from ideal behavior for a gas? Explain your reasoning.

    Yes, polarity does seem to affect the deviation from ideal behavior. Both of the nonpolar gases have real pressures that are very close to those predicted by the Ideal Gas Law. The polar gases, however, show extreme deviations from ideal behavior.

Read This!

According to the assumptions of Ideal Gas Theory, gas molecules have no attraction towards one another. Therefore, the motion of molecules is only in straight lines and there is no preference for moving towards one another, away from one another or into a wall of the container—theoretically. In a real gas, however, the molecules **do** have attraction for one another through intermolecular forces. Therefore, the molecules may have a slight preference for moving towards one another instead of moving towards the wall of the container.

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19. If pressure is determined by the number of times and the force with which a gas molecule collides with the walls of the container, how will the attractions between gas molecules affect the pressure—will the observed pressure be higher or lower than that predicted by the Ideal Gas Law? Explain your reasoning.

    If the gas molecules are attracted to one another, they will collide with the walls of the container less often or with less force. This will lower the pressure, compared to that predicted by the Ideal Gas Law.

20. As the intermolecular forces between gas molecules become stronger, will the deviation between the observed pressure and predicted pressure increase or decrease? Explain your reasoning.

    As the intermolecular forces become stronger between molecules, the deviation from ideal behavior will increase because the gas molecules will collide with the sides of the container less often.

21. As the volume of the container gets larger and the gas molecules move farther apart on average, will the effect of intermolecular forces cause a greater or lesser deviation on the pressure of the gas? Explain your reasoning.

    As the volume of the container becomes larger, the effect of intermolecular forces should decrease. The increased distance between gas molecules will make the attractive forces less pronounced, so the gas molecules will collide with the sides of the container at a frequency that is closer to ideal.

22. Consider the graph in Model 3. Are your answers to Questions 19–21 supported by the data in Model 3? Provide specific evidence from the graph to justify your answer.

    a. In Question 19, we said intermolecular forces should cause the pressure to be __________ than predicted. Is this observed in Model 3?

    Except for hydrogen, which has nearly zero intermolecular forces, all of the gases in Model 3 have a real pressure that is lower than that predicted by the Ideal Gas Law. This is consistent with the answer to Question 19.

    b. In Question 20, we said the deviation from ideal pressure should __________ as the intermolecular forces get stronger. Is this observed in Model 3?

    The graph in Model 3 shows that as intermolecular forces increase, deviation from ideal behavior also increases. This is consistent with the answer to Question 20.

c. In Question 21, we said the deviation from ideal pressure should ________ as the volume of the container gets larger. Is this observed in Model 3?

The graph in Model 3 shows that as the volume of the gas container increases, the amount of deviation from ideal behavior decreases. This is consistent with the answer to Question 21.

23. Consider the graph in Model 1. Is your answer to Question 20 supported by the data in Model 1? Provide specific evidence from the graph to justify your answer.

Yes, Model 1 supports the answer to Question 20. Even noble gases have weak dispersion forces. As the atoms get larger, and contain more electrons, the dispersion forces increase, and the difference between ideal and real volumes increases. Therefore, krypton should have greater intermolecular forces, and a greater deviation from ideal behavior than the other noble gases shown.

24. All of the gases below have observed pressures that are lower than that predicted by the Ideal Gas Law at all volumes. Rank the gases in order of smallest deviations from ideal behavior to greatest deviations from ideal behavior. Justify your reasoning.

N_2 O_2 F_2 Cl_2

All of the gases are nonpolar, however dispersion forces will increase as the molecules get larger. As the dispersion forces increase so too does deviation from ideal behavior.

25. Considering both the effect of volume and the effect of intermolecular forces, how would the deviation from ideal behavior for a gas change when more moles of gas are introduced into a rigid container? Justify your reasoning.

If more moles of gas are introduced into a rigid container, the percent volume occupied by atoms would increase. In addition, the increased concentration of gas molecules would allow for more intermolecular interaction. Both of these factors would lead to a larger deviation from ideal behavior.

26. Considering both the effect of volume and the effect of intermolecular forces, how would the deviation from ideal behavior for a gas change when the gas is at a higher temperature? (Assume a rigid container.) Justify your reasoning.

An increase in temperature would not change the volume occupied by the gas molecules. However, the effect of intermolecular forces would decrease as the kinetic energies of the molecules increase. Therefore, the deviation from ideal behavior would decrease at higher temperatures.

Extension Questions

Model 4 – Van der Waals Equation

	a ($L^2 \cdot atm/mole^2$)	*b* (L/mole)
He	0.0341	0.0237
N_2	1.39	0.0391
CO_2	3.5900	0.0427
NH_3	4.1700	0.0370

$$P = \frac{nRT}{V - \boxed{nb}} - \boxed{\frac{n^2a}{V^2}}$$

27. The Van der Waals equation is basically the Ideal Gas Law equation with some correction factors. The constants *a* and *b* are proportional to the effects of volume and intermolecular forces that cause the deviations from ideal behavior. These constants are derived by fitting a mathematical model to real data.

    a. Look at the Van der Waals equation in Model 4. The Ideal Gas Law is in there. Circle the terms that make up the Ideal Gas Law.

    See Model 4.

    b. Draw squares around the two correction factors in the Van der Waals equation.

    See Model 4.

28. One of the Van der Waals constants is related to the reduction of usable volume because the molecules of gas take up space. Which correction factor and which constant adjusts for this loss of usable space?

    The correction factor "–nb" in the denominator of the first term reduces the volume of the gas to correct for the volumes of the gas molecules in the container. Therefore, the constant b *is related to the size of the molecules.*

29. The other Van der Waals constant is related to the reduction of pressure due to attractive forces between gas molecules. Which correction factor and which constant adjusts for the loss in pressure?

    The correction factor " $-\frac{n^2a}{V^2}$ *" (the second term) reduces the pressure to correct for the intermolecular attractions between gas molecules. Therefore, the constant* a *is related to the intermolecular forces.*

30. Consider the constants *a* and *b* for carbon dioxide (CO_2) and ammonia (NH_3). Ammonia has a larger *a* constant than CO_2, but a smaller *b* constant. Explain why this is so.

    Carbon dioxide is a larger molecule, so it makes sense that b *is larger for* CO_2*. Ammonia is polar however, and carbon dioxide is not. Ammonia molecules have strong hydrogen bonds causing a strong attraction between molecules in the gas phase. Carbon dioxide molecules interact through weaker dispersion forces. Therefore, the* a *constant is larger for ammonia because is has stronger intermolecular forces.*

31. A 10.000-L tank of nitrogen contains 4.000 moles of gas at 22.00 °C.

a. Calculate the pressure that would be expected if neon was an ideal gas.

$$P = \frac{nRT}{V} = \frac{(4.000\,\text{moles})(0.082057\frac{L\cdot atm}{mole\cdot K})(295.15\,K)}{10.000\,L} = 9.688\,atm$$

b. Calculate the actual pressure using the Van der Waals equation.

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

$$\frac{(4.000\,\text{moles})(0.082057\frac{L\cdot atm}{mole\cdot K})(295.15\,K)}{10.000\,L - (4.000\,\text{moles})(0.0391\frac{L}{mole})} - \frac{(4.000\,\text{moles})^2(1.39\frac{L^2\cdot atm}{mole^2})}{(10.000\,L)^2}$$

$$= 9.84\,atm - 0.2224\,atm$$

$$= 9.62\,atm$$

c. How precise would the anemometer on the tank need to be to detect a deviation from the pressure calculated with the Ideal Gas Law?

The predicted pressure and the real pressure (as calculated by the Van der Waals equation) differ by only several hundredths of an atmosphere. Therefore, the anemometer would need to have a precision of ±0.07 atm in order to detect the deviation. Otherwise the difference in the pressure reading may be seen as an uncertainty in the pressure reading rather than a real difference.

Teacher Resources – Deviations from the Ideal Gas Law

Learning Objectives

1. Explain why deviations in gas properties from those predicted by the Ideal Gas Law are larger at lower volumes, lower temperatures and higher concentrations.
2. Rank a set of gases from largest deviation to smallest deviation based on differences in molecular volume.
3. Rank a set of gases from largest deviation to smallest deviation based on differences in intermolecular forces.

Prerequisites

1. Students should be familiar with the relationships between the gas variables of volume, pressure, moles and temperature. They should be very comfortable with the Ideal Gas Law in both a qualitative and quantitative sense.
2. Students should understand the Kinetic Molecular Theory as it pertains to gas molecule behavior.
3. Students should be able to predict the polarity of molecules and discuss the strength of intermolecular forces when comparing different substances.
4. Students should be able to calculate the volume of a spherical solid using the equation $V = \frac{4}{3}\pi r^3$.

Assessment Questions

1. Which of the following would explain observed gas pressures that were higher than those predicted by the Ideal Gas Law?

   a. Real gas molecules may condense into small vapor droplets.

   b. Real gas molecules are not infinitely small.

   c. Real gas molecules exhibit intermolecular attractions.

   d. Real gas molecules have inelastic collisions with the walls of the container.

2. Of the four gases below, which gas would have the largest deviation from ideal behavior?

   a. HCl *b.* HBr *c.* HF *d.* H_2

3. There are two factors that cause real gases to have pressures that deviate from the ideal pressure calculated by the Ideal Gas Law. Discuss these two factors and how they cause deviations.

Assessment Target Responses

1. *b.*
2. *c. (Owing to the potential for hydrogen bonding.)*
3. *Real gas molecules have volume. This reduces the amount of available space in a gas container, which then causes the real pressure to be higher than that predicted by the Ideal Gas Law. Real gas molecules also have intermolecular forces that cause attraction between the molecules. This causes the molecules to hit the sides of the container less often causing the real pressure to be lower than that predicted by the Ideal Gas Law.*

Teacher Tip

- Question 5 in this activity is meant to generate a good deal of discussion within groups. This is a good place to stop the class and have groups report out. It is important at this point to refrain from correcting analysis as the instructor. As students work through the activity, they will come to realize that the major factors that cause real gases to deviate from ideal behavior are the volume occupied by atoms or molecules and the attractive forces between atoms or molecules.

Alignment with AP Chemistry Framework

- **Essential Knowledge 2.A.2:** The gaseous state can be effectively modeled with a mathematical equation relating to various macroscopic properties. A gas has neither a definite volume nor a definite shape; because the effects of attractive forces are minimal, we usually assume that the particles move independently.

  Learning Objective 2.4 The student is able to use KMT and concepts of intermolecular forces to make predictions about the macroscopic properties of gases, including both ideal and nonideal behaviors.

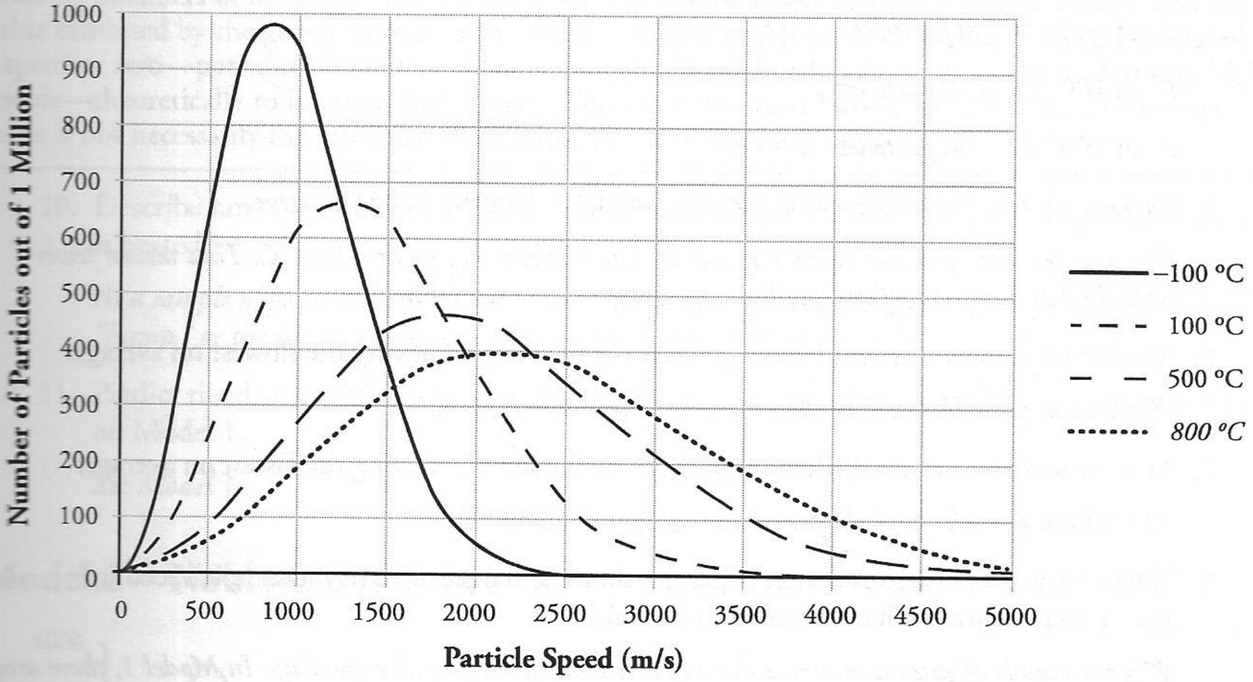
Maxwell-Boltzmann Distributions

How does temperature change the speed of gas particles?

Why?

When a sample of matter is heated, the particles speed up. But what does that mean? Are all the particles in a sample moving at the same speed? Do they all speed up equally? Does mass affect particle speed? Two scientists, James Maxwell and Ludwig Boltzmann, proposed an equation that could be used to predict the speeds of ideal gas particles (atoms or molecules) at any temperature. Their equation is based on statistics and thermodynamic relationships. It is used by chemists and physicists to predict properties of gases such as pressure and diffusion rates, and it can be used to predict rates of reactions involving gases.

Model 1 – Helium at Different Temperatures



1. Consider the graph in Model 1.
   - *a.* What is the variable and unit of the *x*-axis?

     The x-axis is particle speed in meters per second.
   - *b.* Particles of what substance are represented in the graph?

     This graph represents particles of helium.
   - *c.* How many particles are represented in the graph?

     The graph represents one million particles.
   - *d.* What temperatures are represented in the graph?

     The lines on the graph represent −100 °C, 100 °C and 500 °C.

2. According to Model 1, do all of the gas particles in a sample move at the same speed for a given temperature? Justify your answer with evidence from Model 1.

   No, the graph shows a range of speeds for the particles at one temperature. For example, at −100 °C particles can have speeds from 0 to 2500 m/s.

3. According to Model 1, approximately how many gas particles in the sample are traveling 1000 meters per second?

   a. at −100 °C? *900 particles*

   b. at 100 °C? *600 particles*

   c. at 500 °C? *300 particles*

4. According to Model 1, approximately how many gas particles in the sample are traveling 2500 meters per second?

   a. at −100 °C? *0 particles*

   b. at 100 °C? *150 particles*

   c. at 500 °C? *350 particles*

5. Explain why the 500 °C curve is flatter in Model 1 than the −100 °C curve.

   The particles have a wider range of speeds at 500 °C than they do at −100 °C. That means fewer particles can have each of the speeds since more speeds are represented.

6. At what temperature are the helium particles in the sample moving the slowest on average?

   The helium particles have the slowest average speed at −100 °C.

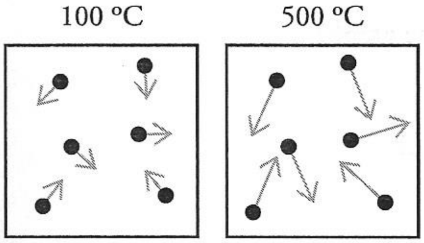
7. At what temperature are the helium particles in the sample moving the fastest on average?

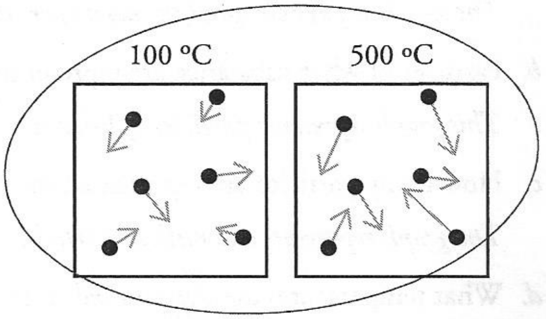
   The helium particles have the fastest average speed at 500 °C.

8. When a sample of gaseous matter is heated, do all of the particles in the sample speed up? Justify your answer with evidence from Model 1.

   When a sample of gaseous matter is heated, only some of the particles speed up. In Model 1, there are slow moving particles at all three temperatures.

9. Circle the set of drawings below that more accurately illustrates the difference in particle speeds for particles of helium at 100 °C and 500 °C? Justify your reasoning. *Hint:* The longer the arrow, the faster the particles is moving.

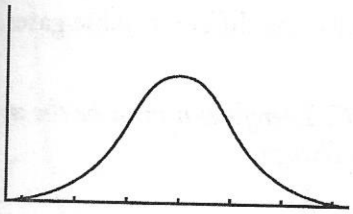




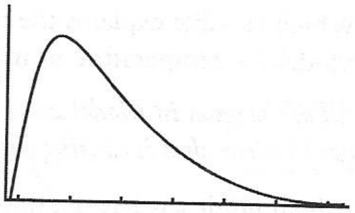
   Regardless of temperature, particles will assume a range of speeds. Not all will be fast or slow. Rather, the percentage of "fast" particles will increase as the temperature increases.

Read This!

The distribution curves in Model 1 are based on the mathematical equation developed by Maxwell and Boltzmann. Their shape is generally a bell curve, but they are skewed to the right.



Normal bell curve



Right-skewed bell curve

Bell curves are used by mathematicians to model the properties of large groups of things. There will always be some variation to the property, but values in the middle of that range tend to be exhibited more often by members of the group than the extremes. On a normal bell curve, the average value is also the value exhibited by the group most often. The left edge of Maxwell-Boltzmann distributions are limited by a speed of zero—particles cannot have negative speeds. The right edge, however, can extend to very high speeds—theoretically to infinitely high speeds. This causes the distribution to be skewed. The average value is not necessarily the value that is exhibited by the group most often.

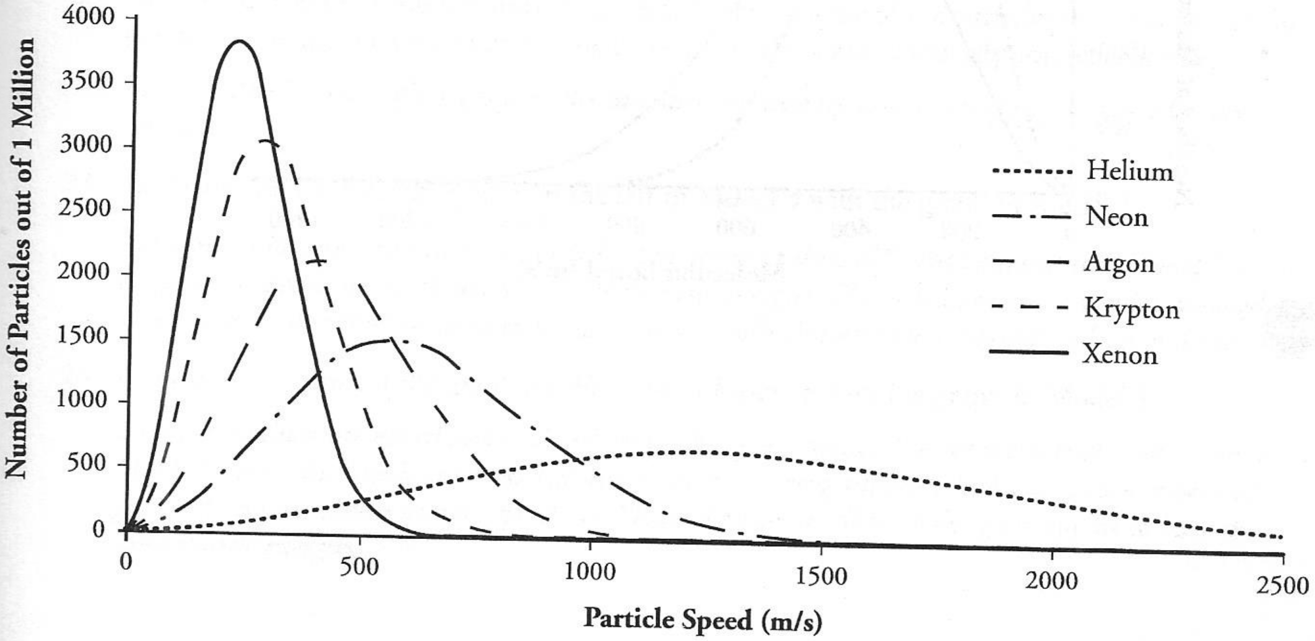
10. Describe how the distribution curve for the speeds of particles in a sample changes as the sample is heated.

    As a sample of gas is heated, the distribution of particle speeds shift to the right—to higher speeds. The "hump," or the curve's maximum value on the y-axis, shifts to the right.

11. Predict the distribution curve for a sample of helium at a temperature of 800 °C. Draw this curve on Model 1.

    See Model 1.

Model 2 – Noble Gases at 100 °C



12. List the noble gases that are represented in the graph in Model 2 with their average atomic masses.

Helium, 4.00 amu
Argon, 39.95 amu
Xenon, 131.29 amu
Neon, 20.18 amu
Krypton, 83.80 amu

13. Which variable explains the difference in distribution curves for the different noble gases in Model 2—temperature or mass? Explain your reasoning.

All of the gases in Model 2 are at the same temperature—100 °C. Therefore, it must be the mass of the gas particles that is causing the distributions of particle speeds to change.

14. Which noble gas has the slowest average particle speed at 100 °C?

Xenon has the slowest average speed.

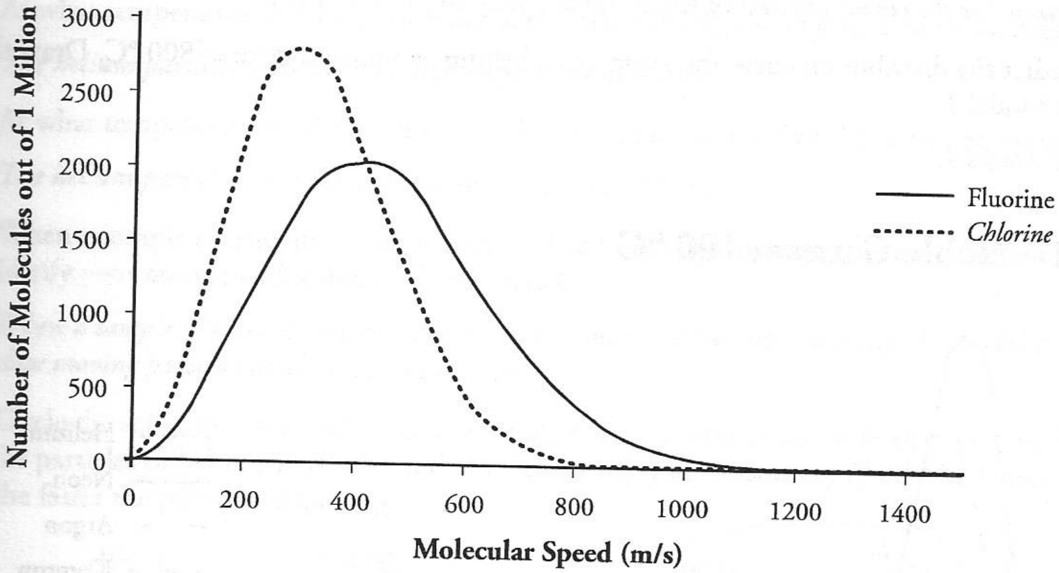
15. Which noble gas has the fastest average particle speed at 100 °C?

Helium has the fastest average speed.

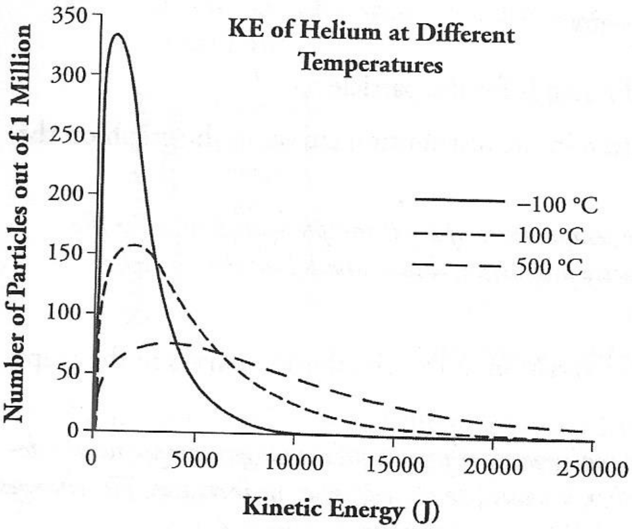
16. In a complete sentence, describe the relationship between the molar mass of particles in a sample and the average particle speed at a given temperature.

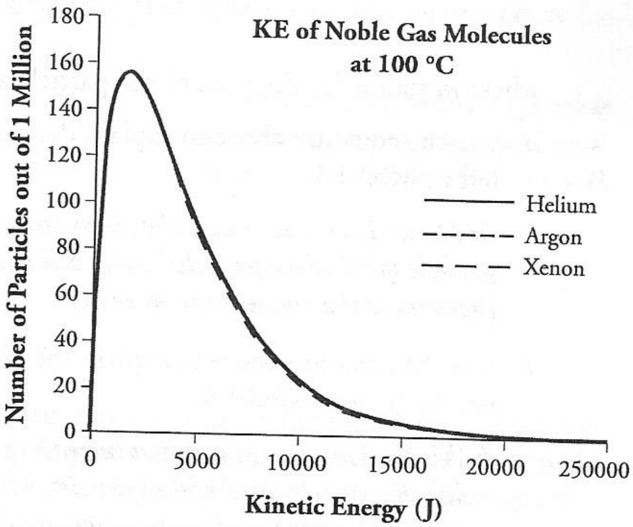
As the molar mass of the gas particles increases, the average particle speed decreases when samples are compared at the same temperature.

17. Consider the distribution curve below for fluorine gas (F_2) at 100 °C. Sketch an approximate distribution curve for chlorine gas (Cl_2) at 100 °C on the same graph.



Model 3 – Kinetic Energies





18. What is the variable and unit of the *x*-axis for both of the graphs in Model 3?

    The x-axis *is kinetic energy in Joules.*

19. What variable, temperature or molar mass, is being varied in the graph on the left?

    The graph on the left shows the effect of temperature on the kinetic energy of the particles.

20. What variable, temperature or molar mass, is being varied in the graph on the right?

    The graph on the right shows the effect of molar mass on the kinetic energy of the particles.

21. Describe the relationship between the average kinetic energy of the particles in a sample and the temperature when the molar mass is held constant. Use a grammatically correct sentence.

    As the temperature of the gas sample increases, the average kinetic energy of the particles increases.

22. Describe the relationship between the average kinetic energy of the particles in a sample and the molar mass when the temperature is held constant. Use a grammatically correct sentence.

    As the molecular mass of the gas particles increases, the average kinetic energy of the particles stays the same.

23. Compare and contrast the graph on the left in Model 3 with the graph in Model 1.

    Both graphs illustrate the distribution of helium atoms at three different temperatures. Model 1 shows the particle speeds, while Model 3 shows the kinetic energies. The distributions are similar although the kinetic energy distributions tend to be more dramatically skewed from a normal bell curve shape.

24. Compare and contrast the graph on the right in Model 3 with the graph in Model 2.

    Both graphs illustrate distributions of different noble gases. Model 2 shows the particle speeds, while Model 3 shows the kinetic energies. The distributions are very different. In Model 2, the larger noble gas particles have slower average speeds. In Model 3 however, all the noble gases appear to have the same kinetic energies.

25. The kinetic energy of a particle in a sample can be calculated by the following equation:

$$KE = \frac{1}{2}mv^2$$

where m stands for the mass of the particle and v stands for the particle speed.

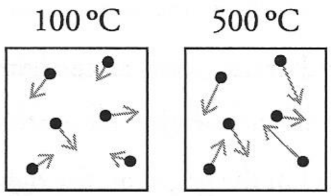
a. Use the equation above to explain the variation in the distribution curves in the graph on the left in Model 3.

In Model 1 we determined that increasing the temperature of a gas sample would increase the particle speed of the particles. Since KE is directly proportional to v, *the KE of the particles increases as the temperature increases.*

b. Use the equation above to explain the lack of variation in the distribution curves in the graph on the right in Model 3.

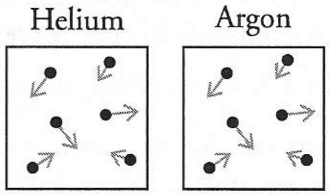
In Model 2 we determined that increasing the molar mass of the particles in a gas sample would decrease the particle speed of the particles. Therefore, v *would be decreasing as* m *increases. The changes in these two variables offset one another so that KE remains constant.*

26. Draw particulate representations of helium atoms at the two different temperatures below. Use arrows to illustrate the distributions in kinetic energies.



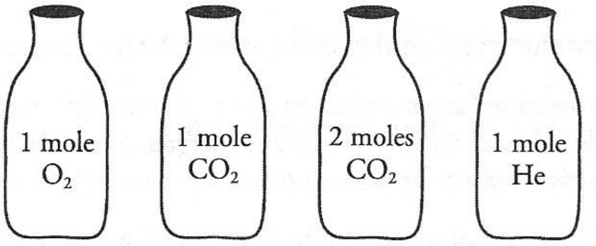
Helium atoms at 500 °C must travel faster, on average, than helium atoms at 100 °C.

27. Draw particulate representations of two different noble gases at the same temperature below. Use arrows to illustrate the distributions in kinetic energies.



The helium and argon atoms will have the same kinetic energy.

28. A student is presented with four bottles containing different gases. All samples are at the same temperature.



a. Which gas sample has the fastest average particle speed?

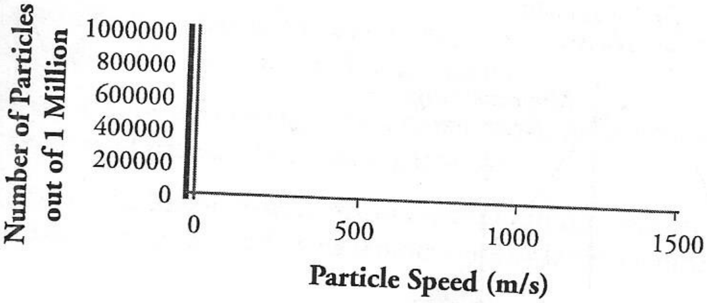
The helium sample will have the fastest average particle speed because it has the lowest molar mass.

b. Which gas sample has the highest average kinetic energy?

All of the gas samples will have the same kinetic energy because they are all at the same temperature.

Extension Questions

29. Theoretically, what would the distribution curve for particle speeds look like for any gas at absolute zero?

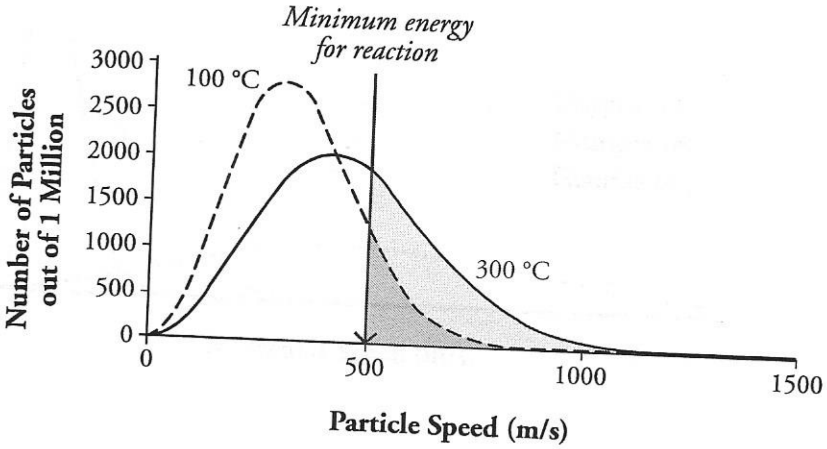


At absolute zero, nearly all particle motion ceases and you would see a line with an infinite slope at y = 0.

30. In Question 28, one of the four bottles contained 2 moles of gas rather than 1 mole. Describe how this might change the gas sample behavior in terms of particle speed distribution, kinetic energies of the particles, pressure on the sides of the bottle and mean free path—the average distance a particle travels before colliding with another particle in the sample.

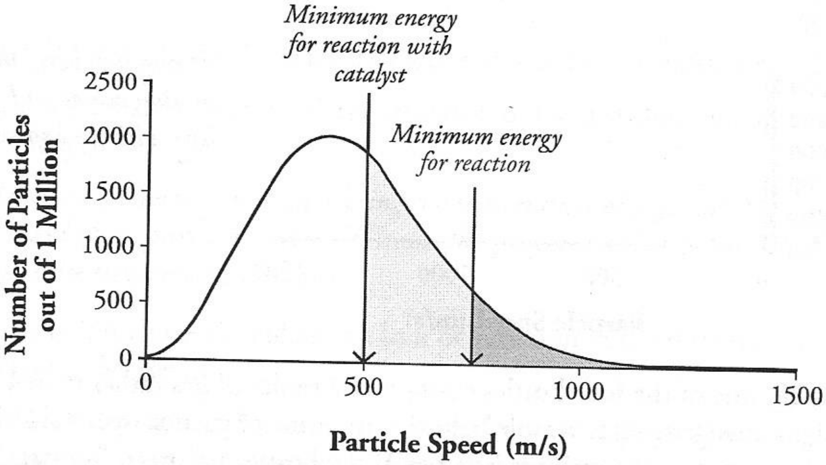
Having 2 moles of gas in the bottle will make things more crowded, but the molecules of a gas are so far apart that the change to many properties would be unnoticeable. The molecules would still have the same average speed (their mass and temperature have not changed), they would still have the same average kinetic energies. Although the total pressure of the gas would be double, each molecule would cause the same average force upon collision. The increased pressure is due to the doubled number of collisions. The only property that would change would be the mean free path. With twice as many molecules it would make sense that the mean free path would be halved—molecules would only be able to move half the distance on average before they collide with another molecule in the sample.

31. The activation energy for a chemical process is the minimum energy needed for a successful reaction to occur. This might be the energy needed to break a bond in a reactant molecule or to ionize a key component in the reaction. The speed with which the reaction occurs is a direct correlation to how many particles in the sample have the minimum energy. Use a Maxwell-Boltzmann distribution to illustrate why raising the temperature of a reactant mixture often speeds up the reaction.



The area under the curve indicates the number of particles that have the minimum energy or more. This area is larger for the distribution curve at 300 °C than it is at 100 °C. Since more particles have the required energy at 300 °C, the reaction will happen faster at that temperature.

32. Use a Maxwell-Boltzmann distribution to illustrate how adding a catalyst (lowering the activation energy) to a reaction speeds up the reaction rate.



The area under the curve indicates the number of particles that have the minimum energy or more. This area is larger when the required energy is lowered. This means more of the collisions will be successful and the rate of reaction will increase.

Teacher Resources – Maxwell-Boltzmann Distributions

Learning Objectives

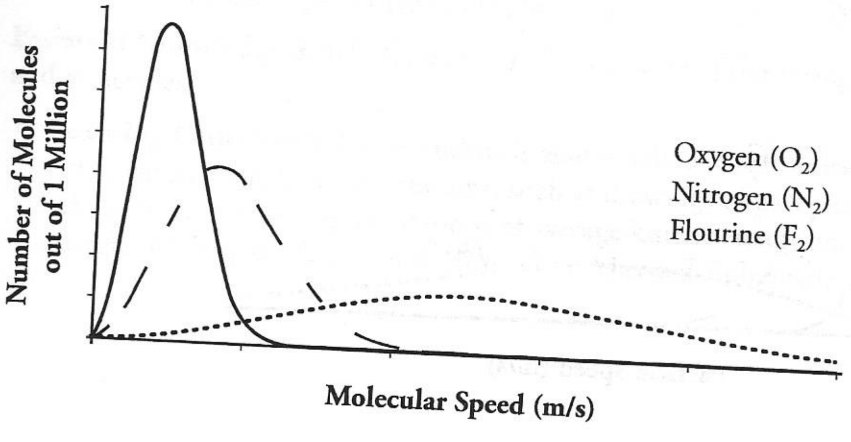
1. Describe the effect of increased temperature on the distribution of particle speeds and kinetic energies of particles in an ideal gas sample.
2. Describe the effect of increased molar mass on the distribution of particle speeds and kinetic energies of particles in an ideal gas sample.
3. Predict the Maxwell-Boltzmann distribution for a gas sample when given a distribution for a similar sample at a different temperature or having a different molar mass.

Prerequisites

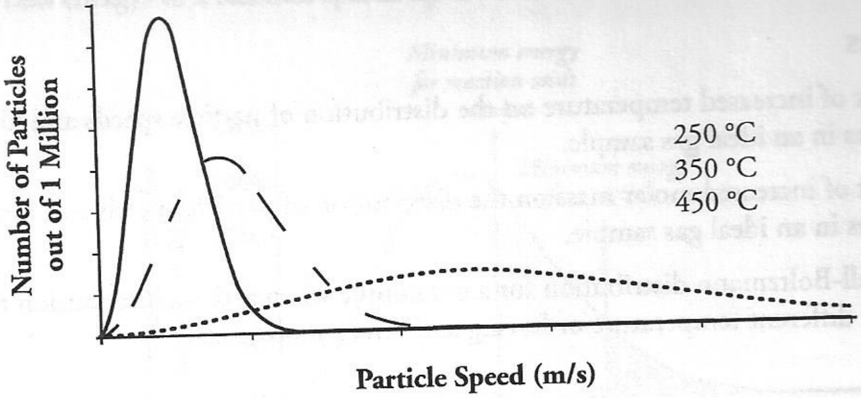
1. Students should be aware that particles in a sample of matter speed up when they are heated.
2. Students should understand that kinetic energy is the energy that a moving object, such as a molecule, exhibits.
3. Students should have a basic knowledge of a "bell curve" distribution.

Assessment Questions

1. Which of the following best describes the speeds of particles in a gas sample?
   a. All particles move at the same speed.
   b. Many particles have a low speed with fewer at higher speeds.
   c. Many particles have the average speed with fewer having low or high speeds.
   d. Many particles have a high speed with fewer at lower speeds.
2. Match each curve in the graph below to a gaseous substance at 100 °C.



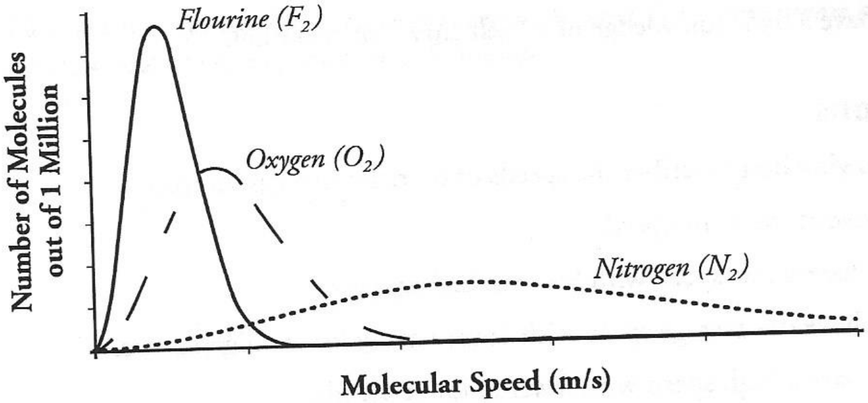
3. Match each curve in the graph below to a temperature for the helium sample.



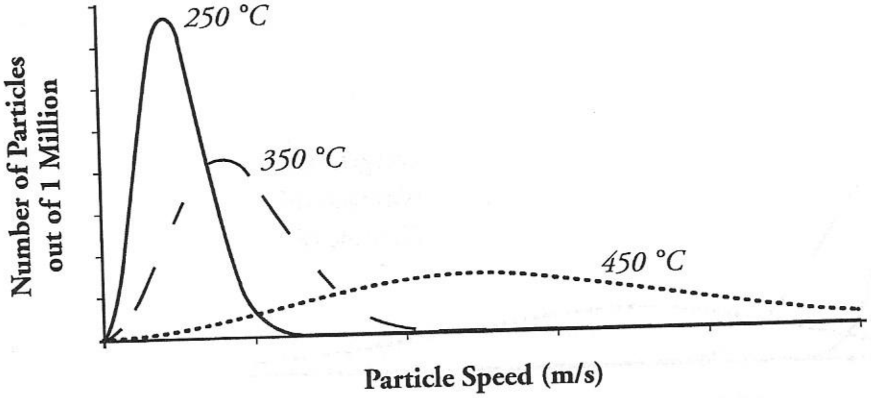
Assessment Target Responses

1. *c*

2.



3.



Teacher Tips

- One of the biggest misconceptions students have about particle motion is that faster particles have higher kinetic energy. Model 3 of this activity makes students confront this misconception by showing the speed and KE graphs side by side. The KE of the particles is only related to the temperature of the particles. This is assessed in Question 29.
- Students often have an unrealistic idea of gas particles in space. They think that doubling the number of particles in a certain volume will affect properties like particle speed and kinetic energy. Help students understand the distance between particles by pointing out the average molecule size and mean free path of a nitrogen molecule in air. At ambient pressures, the mean free path of nitrogen is around 65 µm. The size of the molecule itself however is 106 times smaller—about 70 pm.
- There are several websites that offer molecular motion simulations with Maxwell-Boltzmann distributions. These can be powerful to help students visualize the motions of molecules and how they change with temperature and molecular mass. One example:

  http://phet.colorado.edu/en/simulation/gas-properties

  (Click on "Measurement Tools" and activate the Energy Histograms)

Alignment with AP Chemistry Framework

- **Essential Knowledge 2.A.2:** The gaseous state can be effectively modeled with a mathematical equation relating various macroscopic properties. A gas has neither a definite volume nor a definite shape; because the effects of attractive forces are minimal, we usually assume that the particles move independently.

  Learning Objective 2.5 The student is able to refine multiple representations of a sample of matter in the gas phase to accurately represent the effect of changes in macroscopic properties on the sample.

  Learning Objective 2.6 The student can apply mathematical relationships or estimation to determine macroscopic variables for ideal gases.

- **Essential Knowledge 5.A.1:** Temperature is a measure of the average kinetic energy of atoms and molecules.

  Learning Objective 5.2 The student is able to relate temperature to the motions of particles, either via particulate representations, such as drawings of particles with arrows indicating velocities, and/or via representations of average kinetic energy and distribution of kinetic energies of the particles, such as plots of the Maxwell-Boltzmann distribution.

Heats of Formation

What do the tabulated ΔH°_f values in the appendix of my textbook mean?

Why?

Enthalpies of formation, ΔH°_f, are commonly tabulated in chemistry texts and reference materials. They are the most common way of calculating theoretical ΔH° values via Hess's law, but often the reaction that they refer to is not shown in the table. In this activity, we will explore these values, what they represent and how they can be used to predict the enthalpies of other reactions.

Model 1 – Comparing Reactions

Set A

Formation Reactions	ΔH°_f (kJ/mole)
$\frac{3}{2}O_2(g) + 2Al(s) \rightarrow Al_2O_3(s)$	–1675
$6C(\text{graphite}) + 6H_2(g) + 3O_2(g) \rightarrow C_6H_{12}O_6(s)$	–6984
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	–286
$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$	+33
$\frac{1}{2}H_2(g) + C(\text{graphite}) + \frac{1}{2}N_2(g) \rightarrow HCN(g)$	+131

Set B

Not Formation Reactions	ΔH° (kJ/mole)
$3O_2(g) + 4Al(s) \rightarrow 2Al_2O_3(s)$	–3350
$CO_2(g) + H_2O(l) \rightarrow C_6H_{12}O_6(s)$	+2805
$2H(g) + O(g) \rightarrow H_2O(l)$	–1121
$H^{1+}(aq) + OH^{1-}(aq) \rightarrow H_2O(l)$	–231
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	–114

1. Consider the reactions in Model 1. What type of reaction are all of the examples in Model 1—synthesis, decomposition, single replacement, double replacement or combustion?

   Synthesis.

2. Compare the first reaction in each set (producing aluminum oxide).

   a. How are the reactions similar?

   Both reactions produce aluminum oxide. Both reactions use oxygen gas and solid aluminum as reactants.

   b. How are the reactions different?

   The coefficients for the reaction in Set B are double the coefficients for the reaction in Set A.

3. Compare the two sets of reactions in Model 1.

   a. Which set of reactions uses fractional coefficients to balance the equation, forcing the product to always have a coefficient of one?

   Some reactions in Set A use fractions to balance the equation.

   b. Which set of reactions uses only elements as reactants?

   Set A uses only elements as reactants.

   c. Which set of reactions uses reactants that would not be stable substances (not their natural state)? For example, a single oxygen atom is not a stable entity.

   Some reactions in Set B use reactants that would not be in a stable state.

4. A **formation reaction** is defined as a synthesis reaction where one mole of product is made from component elements in their natural state.

   a. Which set of reactions in Model 1 are formation reactions?

   Set A.

   b. Add a label to Model 1 indicating this set as a group of formation reactions.

   See Model 1.

5. Explain why the following reactions are **not** formation reactions.

   $Mg^{+2}(aq) + 2Cl^{-}(aq) \rightarrow MgCl_2(s)$ *Reactants are ions, not elements in their natural state.*

   $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$ *Reactants contain a compound.*

   $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ *Reaction is not balanced to form 1 mole of product.*

6. The numerical values in Model 1 are standard enthalpies for the reactions. Enthalpies for formation reactions are called standard heats of formation, and they are given the symbol $\Delta H°_f$.

   a. Label the column of enthalpies for the formation reactions $\Delta H°_f$.

   See Model 1.

   b. Label the column of enthalpies for the other reactions $\Delta H°$.

   See Model 1.

7. Are standard heats of formation endothermic, exothermic or both?

   Model 1 shows that some standard heats of formation are endothermic (positive) while others are exothermic (negative).

8. Consider what you know about the energy involved in breaking and forming bonds. Explain why some standard heats of formation might be endothermic?

   Some formation reactions require the breaking of bonds in reactant molecules, e.g., $O_2(g)$ *or* $Al(s)$. *The energy required to break these bonds may be larger than the energy released when the products are formed, making the overall reaction endothermic.*

Read This!

Your chemistry textbook probably has an appendix that tabulates standard heats of formation for many common substances. Rather than show the entire formation reaction, they simply list the compound that is formed. It is assumed that the user understands the reaction represented. Some of the values in the list are found by experiment, others are likely calculated indirectly from other data.

9. Find a table of standard heats of formation in your textbook or online.

   a. What is the ΔH°_f for solid sodium chloride?

   –411 kJ/mole

   b. Write the reaction that involves that energy change.

   $Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$

   c. What is the ΔH°_f for gaseous iodine, $I_2(g)$?

   62.4 kJ/mole

   d. Write the reaction that involves that energy change.

   $I_2(s) \rightarrow I_2(g)$

10. Explain why the ΔH°_f for gaseous oxygen, $O_2(g)$, is zero.

    Oxygen gas is already an element in its natural state, so no energy is needed to produce it.

11. If a formation reaction was reversed, how could the standard enthalpy for that reaction be calculated from a standard heat of formation listed in the table? Illustrate your understanding by finding the ΔH° for the following reaction.

    $$HBr(g) \rightarrow \frac{1}{2}H_2(g) + \frac{1}{2}Br_2(l)$$

    When a reaction is reversed, the ΔH *of the reaction switches sign from positive to negative or vice versa. The* ΔH°_f *of hydrogen bromide is –36 kJ/mole, so the* ΔH° *for this reaction would be +36 kJ/mole.*

12. If a formation reaction was multiplied by a factor, how could the standard enthalpy for that reaction be calculated from a Standard Heat of Formation listed in the table? Illustrate your understanding by finding the ΔH° for the following reaction.

    $$2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$$

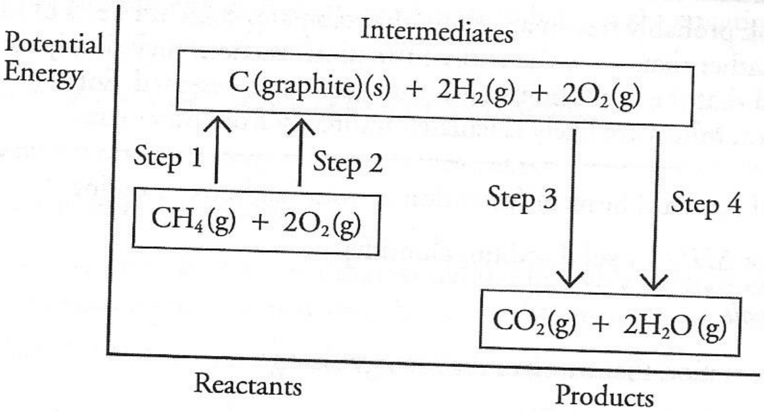
    When a reaction is multiplied by a factor, the ΔH *of the reaction is also multiplied by that factor. The* ΔH°_f *of aluminum chloride is –706 kJ/mole, so the* ΔH° *for this reaction would be –1412 kJ/mole.*

STOP

Read This!

Standard heats of formation can be used to predict the enthalpies of many other reactions. Imagine that a reaction occurs by all reactants decomposing into elements in their natural state and then recombining to form the products. Although very few chemical reactions occur in this manner, it does not really matter. Enthalpy is a **state function**, which means it is determined only by the initial state of the reaction and the final state of the reaction, not the process that occurs in between. The enthalpy change that is calculated for our imaginary process will give us the enthalpy for the real-life reaction. Therefore, several formation reactions (or reverse formation reactions) can be combined using Hess's law to calculate the enthalpy for any reaction.

Model 2 – Calculating an Enthalpy, ΔH°, from ΔH°_f Values



13. Write the reaction for the overall process in Model 2.

    $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

14. Notice that the intermediates in the process in Model 2 are elements in their natural states.

    a. Which steps in the process in Model 2 represent formation reactions, or multiples of formation reactions?

    Steps 3 and 4 are formation reactions.

    b. Which steps in the process in Model 2 represent formation reactions, or multiples of formation reactions, in reverse?

    Steps 1 and 2 are reverse formation reactions.

15. Use a table of standard heats of formation to calculate the energy change when the reactants in Model 2 turn into the intermediates. Be sure to include the correct sign on this energy change.

    $CH_4(g)$ $\Delta H^\circ_f = -75$ kJ/mole $\quad$ $O_2(g)$ $\Delta H^\circ_f = 0$ kJ/mole

    Step 1 + Step 2 = +75 kJ/mole + 2(0 kJ/mole) = +75 kJ/mole

16. Use a table of standard heats of formation to calculate the energy change when the intermediates in Model 2 turn into the products. Be sure to include the correct sign on this energy change.

    $CO_2(g)$ $\Delta H^\circ_f = -394$ kJ/mole $\quad$ $H_2O(g)$ $\Delta H^\circ_f = -242$ kJ/mole

    Step 3 + Step 4 = −394 kJ/mole + 2 moles(−242 kJ/mole) = −878 kJ/mole

17. Use your answers in Questions 15 and 16 to calculate the overall ΔH° for the process in Model 2.

    75 kJ/mole + (−878 kJ/mole) = −803 kJ/mole

18. Use what you have learned from Model 2 to calculate the standard enthalpy, ΔH°, for the following reaction using a table of standard heats of formation. Show all calculations and be prepared to explain your process for solving this problem.

    $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

    $\Delta H^\circ_f = -46$kJ/mole $\quad$ 0 kJ/mole $\quad$ 90 kJ/mole $\quad$ −242 kJ/mole

    ΔH = 4 moles(+46 kJ/mole) + 5 moles(0 kJ/mole) + 4 moles(90 kJ/mole) + 6 moles(−242 kJ/mole) = −908 kJ

Extension Questions

19. The heat of combustion for 1 mole of propane, C_3H_8, at standard conditions is −2,046 kJ.

    a. Write a balanced chemical equation for the combustion of propane.

    $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

    b. Calculate the heat of formation, ΔH°_f, of propane given that the ΔH°_f of gaseous water is −242 kJ/mole and the ΔH°_f of carbon dioxide gas is −394 kJ/mole.

    ΔH°_{comb} = *1 mole(*$-\Delta H^\circ_f$ *propane) + 5 moles(*$-\Delta H^\circ_f$ *oxygen) + 3 moles(*ΔH°_f *carbon dioxide) + 4 moles(*ΔH°_f *gaseous water)*

    −2,046 kJ = 1 mole($-\Delta H^\circ_f$ *propane) + 5 moles(0 kJ/mole) + 3 moles(−394 kJ/mole) + 4 moles(−242 kJ/mole)*

    ΔH°_f *propane = −104 kJ/mole*

20. Which of the two formation reactions below would you predict to have the largest exothermic heat of formation? Justify your reasoning.

$2Al(s) + O_2(g) \rightarrow Al_2O_3(s)$	$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$
ΔH°_f = *−1675 kJ/mole*	ΔH°_f = *−601 kJ/mole*

The heat of formation for aluminum oxide is larger because the Al_2O_3 *crystal lattice is stronger than the MgO crystal lattice. Aluminum has a +3 charge while magnesium only has a +2 charge. The Coulombic attraction between aluminum and oxygen is stronger. The energy needed to break the bonds on the reactant side would be similar—separating the metal atoms in the solid and breaking bonds in the gaseous oxygen atoms.*

Teacher Resources – Heats of Formation

Learning Objectives

1. Identify a formation reaction as a synthesis reaction where one mole of product is made from elements in their natural state.
2. Explain why some formation reactions have a heat of reaction that is endothermic.
3. Use standard heats of formation to calculate the standard enthalpy of a new reaction.

Prerequisites

1. Students should understand the energy changes related to the breaking and forming of bonds—breaking bonds is endothermic, forming bonds is exothermic.
2. Students should be familiar with Hess's law and be able to add several reactions and enthalpies together to calculate the enthalpy of an overall reaction.

Assessment Questions

1. Which of the following reactions is a formation reaction?
   a. $3O_2(g) \rightarrow 2O_3(g)$
   b. $N_2(g) + 2O_2(g) \rightarrow N_2O_4(g)$
   c. $6CO_2(g) + 6H_2O(g) + C_6H_{12}O_6(s) + 6O_2(g)$
   d. $SO_3(g) + H_2O(g) \rightarrow H_2SO_4(g)$
2. Gaseous hydrogen iodide, HI (g), has a $\Delta H°_f$ of 26 kJ/mole. Propose an explanation for why this reaction has a positive heat of formation.
3. Use a table of standard heats of formation to calculate the standard enthalpy of the reaction between solid magnesium chloride and a solution of sodium hydroxide.

Assessment Target Responses

1. *b*
2. *The reaction for the formation of hydrogen iodide would be:* $\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(s) \rightarrow HI(g)$.

   The bonds in both the hydrogen molecules and the iodine molecules (and solid lattice) would need to be broken to form the hydrogen iodide. The sum of these bonds must be greater than the energy released when the hydrogen and iodine bond. Therefore, the heat of formation is positive.
3. $MgCl_2(s) + 2NaOH(aq) \rightarrow 2NaCl(aq) + Mg(OH)_2(s)$

   $\Delta H° = 1\ mole(-\Delta H°_f MgCl_2) + 2\ moles(-\Delta H°_f NaOH) + 2\ moles(\Delta H°_f NaCl) + 1\ mole(\Delta H°_f Mg(OH)_2)$

   $\Delta H° = 1\ mole(+642\ kJ/mole) + 2\ moles(+469\ kJ/mole) + 2\ moles(-407\ kJ/mole) + 1\ mole(-925\ kJ/mole)$

   $\Delta H° = -159\ kJ$

Teacher Tips

- Students will need to refer to a table of standard heats of formation to complete this activity.
- This activity will again make students face their deep rooted misconception that bonds release energy when broken. It may be worth reviewing the correct understanding of energy in relation to bond breaking and forming before this activity. It may even be useful to revisit the reaction of ATP turning into ADP from biology, which seems to be the cause of the misconception. Note that although there is a bond in ATP that breaks to form ADP, there is also a reaction with water that "seals up the ends." It is the bond formed between the ADP and hydroxide and the phosphate and hydrogen that releases the large amount of energy to run life's processes.
- The diagram in Model 2 is used to help students think about an endothermic process to break apart the reactants and an exothermic process when the products are formed. Astute students may point out some inconsistencies with this diagram when it is used in a more general sense. For example, the heat of formation for oxygen is zero, and therefore the up arrow in the diagram should really not be an "up" arrow representing an increase in energy. Likewise, in some cases the heat of formation is endothermic meaning the arrow from reactant to intermediate would go down.

Alignment with AP Chemistry Framework

- **Essential Knowledge 5.C.2:** The net energy change during a reaction is the sum of the energy required to break the bonds in the reactant molecules and the energy released in forming the bonds of the product molecules. The net change in energy may be positive for endothermic reactions when energy is required, or negative for exothermic reactions where energy is released.

  Learning Objective 5.8 The student is able to draw qualitative and quantitative connections between the reaction enthalpy and the energies involved in the breaking and formation of chemical bonds.

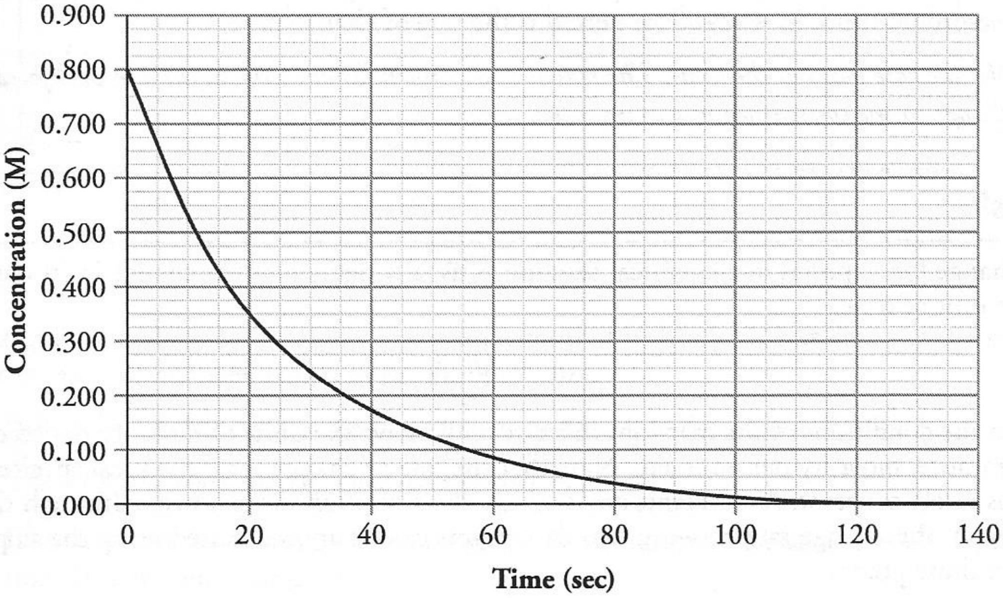
Rate of Reaction

How is the speed of a reaction measured?

Why?

Chemical reactions occur at different speeds. Some are almost instantaneous. Others require patience. For example, rust can form on iron in just a few days or over a period of months depending on the conditions. In order to study the factors that change the speed of a reaction, we must first develop an understanding of how the rate of reaction is monitored during a reaction.

Model 1 – Concentration versus Time Graph



1. The graph in Model 1 illustrates how the concentration of a species in a chemical reaction changes over time.
   a. What unit is the concentration measured in?

   The concentration is measured in molarity.

   b. What unit is the time measured in?

   The time is measured in seconds.

2. Consider the data in Model 1.
   a. What was the concentration of the species when the chemical reaction was initiated?

   The initial concentration of the chemical species in the reaction was 0.80 M.

   b. Did the concentration of the species increase or decrease over time?

   The concentration of the chemical species decreased over time.

   c. Was the species a reactant or product in the reaction? Justify your reasoning.

   The chemical species was a reactant because it was used up during the reaction. Its concentration went down.

3. Consider the data in Model 1.

   a. What was the change in the concentration of the species in Model 1 during the first 10 seconds of the reaction? Include units in your numeric answer.

   In the first 10 seconds, the concentration of the chemical species changed from 0.800 M to 0.525 M. That is a decrease of 0.275 M.

   b. What was the change in the concentration of the species in Model 1 between the 60 and 70 second marks? Include units in your numeric answer.

   During this time segment, the concentration of the chemical species changed from 0.075 M to 0.0500 M. That is a decrease of 0.025 M.

   c. Was the rate of change for this species the same during these two time periods? Justify your reasoning. If no, in which time period is the rate of change faster?

   No, the rate was not the same. The reaction was much faster in the first 10 seconds because a larger change in the concentration was recorded.

Read This!

The rate of change for a species in a chemical reaction is usually defined as the change in its concentration over a specific unit of time.

$$\text{rate} = \frac{\Delta[\ ]}{\Delta t}$$

Depending on the conditions of the reaction, this rate could have the units of molarity per second, molarity per minute, molarity per hour, etc. Note that the rate of change for a chemical species, and for the reaction, is rarely constant. As reactants are used up, the rate often slows down. Although this leads to a curved graph, the average rate between two data points can be approximated using the slope of the graph between those points.

4. Use the data in Model 1 to calculate the average rate of change for the chemical species shown for the following time periods during the reaction. Be sure to include units in your calculation.

   a. The first 10 seconds.

$$\frac{0.550\ M - 0.800\ M}{10\ sec} = -0.025\frac{M}{s}$$

   b. The time between 30 and 40 seconds.

$$\frac{0.15\ M - 0.25\ M}{10\ sec} = -0.010\frac{M}{s}$$

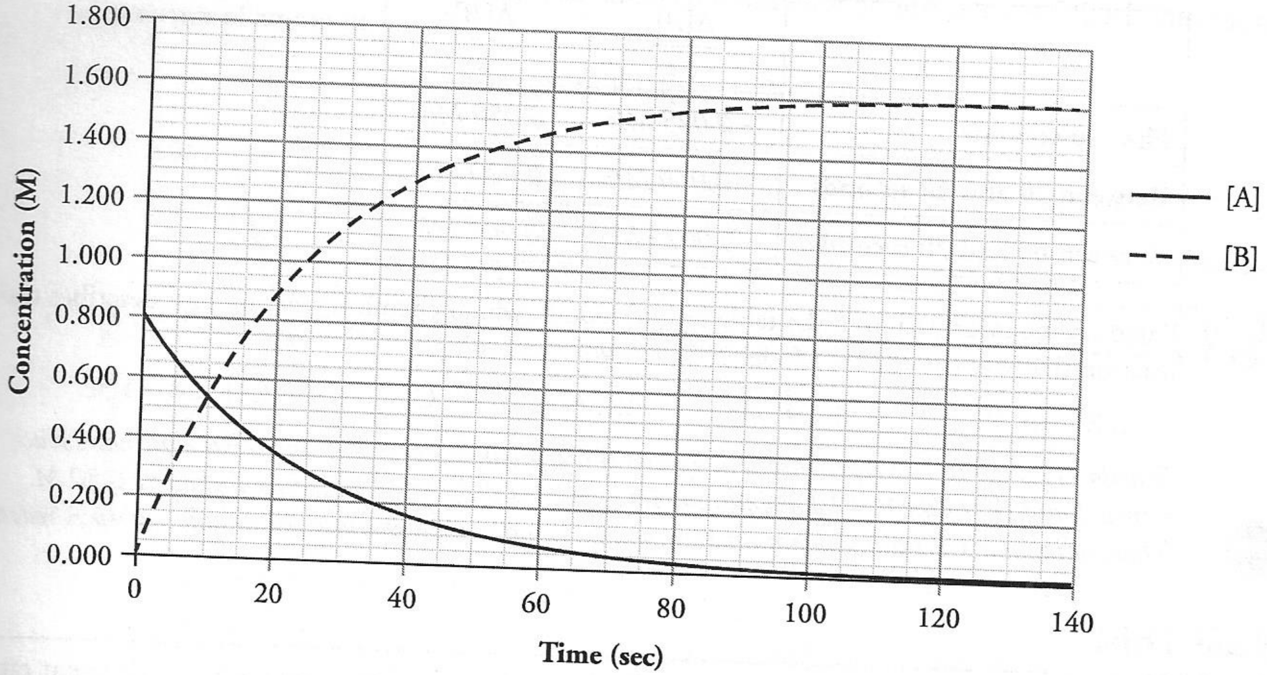
   c. The time between 60 and 70 seconds.

$$\frac{0.050\ M - 0.075\ M}{10\ sec} = -0.0025\frac{M}{s}$$

5. The rates you calculated in Question 4 should be negative values. Why does it make sense that they are negative?

   The concentration of the chemical species is decreasing so the rate should reflect that. A negative value indicates a reduction in the concentration.

Model 2 – Two Species in the Reaction



6. The graph in Model 2 contains the same data as that in Model 1, but data about a second species in the reaction has been added to the graph.

   a. Which line in Model 2 is the same line as in Model 1, the solid or dashed line?

   The solid line represents the same data as that in Model 1.

   b. Does the new data illustrate the change in concentration of a reactant or product of the reaction? Justify your reasoning.

   The new data (the dashed line) represents a product because the concentration is increasing. That indicates that the species is being formed during the reaction.

7. Use the data in Model 2 to calculate the average rate of change for species B for the following time periods during the reaction. Be sure to include units and a sign (+ or –) on your calculation.

   a. The first 10 seconds.

   $$\frac{0.50\ M - 0\ M}{10\ sec} = 0.050\,\frac{M}{s}$$

   b. The time between 30 and 40 seconds.

   $$\frac{1.30\ M - 1.10\ M}{10\ sec} = 0.020\,\frac{M}{s}$$

   c. The time between 60 and 70 seconds.

   $$\frac{1.50\ M - 1.45\ M}{10\ sec} = 0.005\,\frac{M}{s}$$

8. Summarize the calculations you have performed in the previous questions in the table below.

	$\frac{\Delta[A]}{\Delta t}$	$\frac{\Delta[B]}{\Delta t}$
First 10 seconds	*−0.025 M/s*	*0.050 M/s*
Between 30 and 40 seconds	*−0.010 M/s*	*0.020 M/s*
Between 60 and 70 seconds	*−0.0025 M/s*	*0.005 M/s*

9. Based on the information in the table in Question 8, which chemical reaction best describes the reaction that was studied for Model 2? Justify your reasoning.

   I. $2A \rightarrow B$ II. $A \rightarrow 2B$ III. $A + B \rightarrow C$ IV. $A + 2B \rightarrow C$

   Reaction II is the correct representation. Species B is a product, not a reactant. That eliminates reactions III and IV. In the first 10 seconds, species A changes 0.25 M while species B changes 0.50 M. That indicates a 1:2 ratio between the two species. Two times the amount of B is made when A reacts.

Read This!

Depending on the mole ratios of the components of a chemical reaction, you could observe different rates of change for different species. How then can one numerical value for the rate of reaction be determined? By convention, the rate of a reaction is equal to the absolute value of the rate of change for any species that has a coefficient of one in the balanced reaction as written. Think of it as the time needed for the reaction to occur 6.022×10^{23} times.

10. Based on the data in Model 2, what is the initial rate of reaction for the chemical process that was investigated?

    According to the options given in Question 9, species A has a coefficient of one. Therefore, the rate of reaction would be equal to the absolute value of the rate of change for species A.

    The rate of reaction is 0.025 M/s.

11. Consider the following reaction:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Experimental data indicate the initial rate of change for nitrogen is −0.060 M/s.

a. Calculate the initial rate of change for hydrogen.

$$-0.060\,\frac{mol\ N_2}{L \cdot s}\left(\frac{3\ mol\ H_2}{1\ mol\ N_2}\right) = -0.180\,\frac{M}{s}$$

b. Calculate the initial rate of change for ammonia.

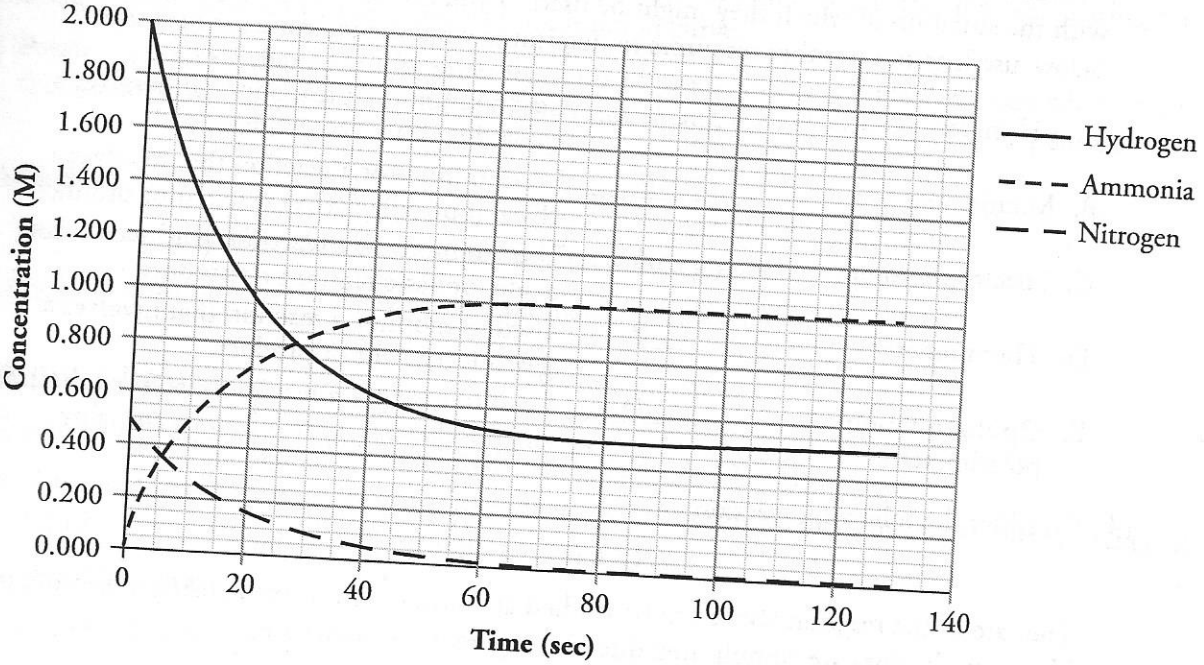
$$-0.060\,\frac{mol\ N_2}{L \cdot s}\left(\frac{-2\ mol\ NH_3}{1\ mol\ N_2}\right) = 0.120\,\frac{M}{s}$$

c. Calculate the initial rate of reaction.

Since nitrogen has a coefficient of one, the rate of reaction would be equal to the absolute value of the rate of change for nitrogen. The initial rate of reaction is 0.060 M/s.

12. The graph below shows the rate of change for hydrogen in the following reaction. Sketch the rate curves for nitrogen and ammonia. The initial concentration of nitrogen is 0.500 M. There is no presence of ammonia initially.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$



Extension Questions

13. In order to gather the data required to produce the graphs in this activity, or any reaction rate graph, an experimenter must be able to quickly measure changes in concentration, either directly or indirectly, of at least one component of a chemical reaction. Match the following lab tools with the situation in which they might be used. If you are not familiar with the instruments below, use Internet or other resources to determine what the instruments measure.

A. pH meter
B. Manometer
C. Spectrophotomer
D. Thermometer
E. Optical rotation polarimeter

___*C*___ Used to monitor a reaction that involves a colored reactant or product.
___*E*___ Used to monitor a reaction that involves a chiral (optically active) reactant or product.
___*A*___ Used to monitor a reaction that involves an acidic or basic reactant or product.
___*B*___ Used to monitor a reaction that involves a gaseous reactant or product.
___*D*___ Used to monitor a reaction that is exothermic or endothermic, with a known enthalpy.

14. Consider the following reaction:

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

The rate of the reaction above can be studied at constant temperature using a pressure probe. However, the data are complicated due to the presence of two gases.

a. If the reaction vessel initially contained only dinitrogen tetroxide, would you expect an overall increase or decrease in pressure as the reaction proceeds? Justify your reasoning.

There would be an overall increase in pressure. Although one unit of dinitrogen tetroxide is being consumed, two units of nitrogen dioxide are being produced. Therefore, a net gain in gaseous moles and pressure will be measured.

b. Suppose the above reaction showed an increase of 0.500 kPa in 10 seconds. What would be the change in pressure for dinitrogen tetroxide in the same time period?

The pressure of dinitrogen tetroxide would decrease 0.250 kPa in the same time period.

Teacher Resources – Rate of Reaction

Learning Objectives

1. Determine the rate of change for a reactant or product in a chemical reaction by calculating the average slope between two data points for a reaction curve.
2. Predict the rate of change for the other reactants or products in a chemical reaction when given the rate of change for one component in the reaction and the balanced chemical equation.

Prerequisites

1. Students must be able to find the slope of a line from a graph.
2. Students must be comfortable with stoichiometric calculations.

Assessment Questions

1. Consider the following reaction: $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

   If the initial rate of change for sulfur dioxide is –2.00 M/min, what is the initial rate of change of oxygen?

   a. –4.00 M/min

   b. –1.00 M/min

   c. 4.00 M/min

   d. 1.00 M/min

2. Consider the following reaction: $N_2(g) + 3Cl_2(g) \rightarrow 2NCl_3(g)$

   If the rate of reaction is 0.750 M/s, what is the rate of change of chlorine?

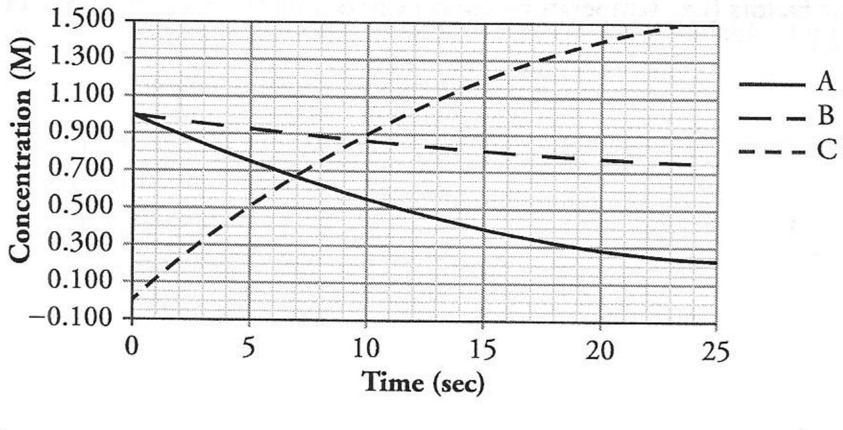
   a. 0.250 M/s

   b. 2.250 M/s

   c. –0.250 M/s

   d. –2.250 M/s

3. Consider the following rate graph. Write a chemical equation for the reaction that was investigated based on the rates of change for each species in the reaction.



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   b. 2.250 M/s

   c. –0.250 M/s

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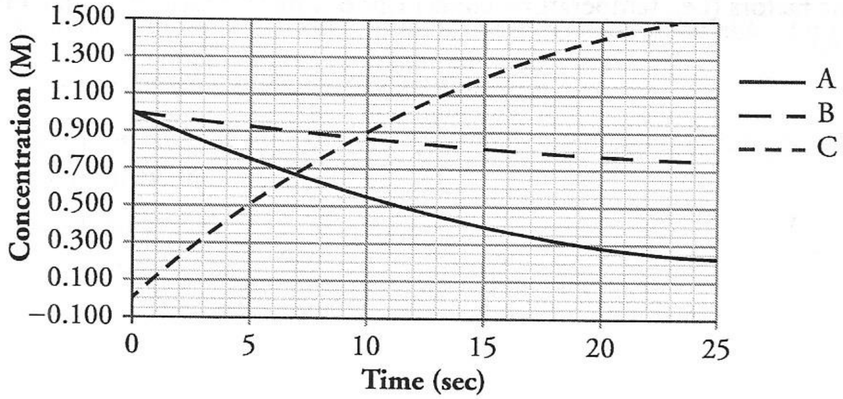


Assessment Target Responses

1. *b*
2. *d*
3. $A + 2B \rightarrow 3C$

Teacher Tips

- Before you begin this activity with students, make sure they have a solid understanding of what is meant by "rate." Ask them to write the units that might be used to measure the rate (speed) of a vehicle, the growth of a tree, a leaky faucet or how fast they read. Emphasize that in all cases something is measured versus time. The unit of time may change depending on how fast or slow the rate is. For example, tree growth is probably measured "per year" while reading may be measured "per minute." Ask students how they might measure the rate of a chemical reaction.
- Students often have difficulty knowing when to multiply or divide by a coefficient in a chemical reaction when trying to determine the rate of change of one species from another. It may help to point out that they can use the mole ratio between species as a conversion factor for the rate of change.
- It is also confusing to many students why the rate of a reaction would be defined as the absolute value of the rate of change for a chemical with a coefficient of one. What if there is no species in the reaction with a coefficient of one? Emphasize that you are finding the rate in which the reaction occurs 6.022×10^{23} times. Students can once again use the mole ratio between moles of a reactant or product and moles of the reaction—the coefficient of the reaction always being one.

  Example: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

  Calculate the rate of reaction if the rate of change for hydrogen is 0.120 M/s.

  $$\left(\frac{0.120\ mol\ N_2}{s}\right)\left(\frac{1\ mol\ Rxn}{3\ mol\ H_2}\right) = 0.040\frac{M}{s}$$

Alignment with AP Chemistry Framework

- **Essential Knowledge 4.A.1:** The rate of a reaction is influenced by the concentration or pressure of reactants, the phase of the reactants and products, and environmental factors such as temperature and solvent.

  Learning Objective 4.1 The student is able to design and/or interpret the results of an experiment regarding the factors (i.e., temperature, concentration, surface area) that may influence the fate of a reaction.

Method of Initial Rates

How can you use rate data to determine the order of a reaction?

Why?

In most cases, the rate law for a chemical reaction cannot be derived theoretically. If the reaction is a multi-step reaction, the rate law does not correspond to the balanced chemical equation. Finding the rate law would be simple if we could observe the reactions at the molecular level, but that is not possible. We must use indirect evidence. There are many experimental techniques that can be used to determine the rate law for a reaction. Determining the initial rate of a reaction and seeing how that initial rate changes when the concentrations of reactants are changed is one way of using experimental data to determine the rate law.

Model 1 – The Effect of Exponents

$y = kx^n$

where $k = 5$

x	If $n = 0$, then $y = ?$	If $n = 1$, then $y = ?$	If $n = 2$, then $y = ?$
1	*5*	*5*	*5*
2	*5*	*10*	*20*
3	*5*	*15*	*45*
4	*5*	*20*	*80*

1. Consider the mathematical equation in Model 1.

   a. What letter represents a constant in the equation?

   The letter k *is the constant.*

   b. What is the value of the constant?

   The constant k *is equal to 5.*

   c. What letter represents the exponent in the equation?

   The letter n *is the exponent.*

   d. Does x in the equation represent the independent variable, dependent variable or a constant?

   The x *variable is the independent variable.*

2. Fill in the table in Model 1 using the mathematical equation provided. Divide the work among group members.

   See Model 1.

3. Refer to Model 1. Use complete sentences to describe the change in y as x increases when $n = 0$. Justify the pattern you see using your knowledge of mathematics.

   When the exponent is zero, there is no change in y *when* x *changes. This is because any number raised to the zero power is equal to one. Therefore* y *will always equal the constant.*

4. Refer to the column in the Model 1 table where $n = 1$.

   a. When x doubles, what happens to y?

   When x *doubles,* y *also doubles.*

   b. When x triples, what happens to y?

   When x *triples,* y *also triples.*

5. Use a complete sentence to describe the change in y as x increases when $n = 1$. Justify the pattern you see using your knowledge of mathematics.

   When the exponent is one, the change in y *is proportional to the change in* x. *Any number raised to the power of one is itself. Therefore* y *will be the constant multiplied by* x.

6. Refer to the column in the Model 1 table where $n = 2$.

   a. When x triples, what happens to y?

   When x *triples,* y *is multiplied by 9 (3^2).*

   b. When x quadruples, what happens to y?

   When x *quadruples,* y *is multiplied by 16 (4^2).*

7. Use a complete sentence to describe the change in y as x increases when $n = 2$. Justify the pattern you see using your knowledge of mathematics.

   When the exponent is 2, the change in y *is proportional to the change in* x^2. *This is an exponential relationship.*

8. Consider the data below and determine the value of the exponent q. Justify your answer with an explanation or a mathematical equation.

   $r = st^q$

t	r
5	15
10	30
15	45

   When t *is doubled,* r *is doubled, so the exponent* q *is equal to 1.*

   $$\frac{5}{10} = \left(\frac{15}{30}\right)^{q} \qquad \frac{1}{2} = \left(\frac{1}{2}\right)^{q} \qquad q = 1$$

9. Solve for the constant s in Question 8 above.

   $$15 = s(5) \qquad s = \frac{15}{5} = 3$$

10. Consider the data below and determine the value of the exponent q. Justify your answer with an explanation or a mathematical equation.

$r = st^q$

t	r
10	3
20	3
30	3

When t *is doubled,* r *is unchanged so the exponent* q *is equal to 0.*

$\frac{3}{3} = \left(\frac{10}{20}\right)^q \qquad 1 = \left(\frac{1}{2}\right)^q \qquad q = 0$

11. Consider the data below and determine the value of the exponent q. Justify your answer with an explanation or a mathematical equation.

$r = st^q$

t	r
2	12
4	48
6	108

When t *is doubled,* r *is quadrupled so the exponent* q *is equal to 2.*

$\frac{12}{48} = \left(\frac{2}{4}\right)^q \qquad \frac{1}{4} = \left(\frac{1}{2}\right)^q \qquad q = 2$

12. Solve for the constant s in Question 11 above.

$12 = s(2)^2 \qquad s = \frac{12}{4} = 3$

Model 2 – Decolorization of a Dye

rate = k[dye]^n

where k = 3.40×10^3

[dye]	If n = 0, then rate = ?	If n = 1, then rate = ?	If n = 2, then rate = ?
0.10 M	*3.40×10^3 M/s*	*340 M/s*	*34 M/s*
0.20 M	*3.40×10^3 M/s*	*680 M/s*	*136 M/s*
0.30 M	*3.40×10^3 M/s*	*1020 M/s*	*306 M/s*

13. Identify the reactant in the process being studied in Model 2.

    The dye is the reactant in the process.

14. Refer to Model 2.

    a. Circle the rate law for the decolorization of a dye in Model 2.

    See Model 2.

    b. What variable represents the constant in the rate law?

    The variable k *represents the constant in the rate law.*

    c. What variable represents the order of the reaction?

    The variable n *represents the order of the reaction.*

15. Fill in the table in Model 2. Divide the work among group members. *Note:* The unit for rate should be "molarity per second" in all cases.

    See Model 2.

16. How does the initial rate of reaction change as the concentration of the reactant increases when the order of the reaction is zero?

    When the order of the reaction is zero, the initial rate of reaction is unchanged by changes in the concentration of the reactant.

17. How does the initial rate of reaction change as the concentration of the reactant increases when the order of the reaction is one?

    When the order of the reaction is one, the initial rate of reaction changes proportionally to changes in the concentration of the reactant.

18. How does the initial rate of the reaction change as the concentration of the reactant increases when the order of the reaction is two?

    When the order of the reaction is two, the initial rate of reaction changes proportionally to the square of changes in the concentration of the reactant.

19. Consider the data below.

rate = $k[O_3]^n$

$[O_3]$	Initial Rate
0.44 atm	0.01848 atm/min
0.88 atm	0.03696 atm/min

a. Determine the order of the reaction with respect to ozone. Justify your answer with an explanation or a mathematical equation.

When the concentration of ozone is doubled, the initial rate doubles, so the order of reaction with respect to ozone is 1.

$$\frac{0.01848\,\frac{atm}{min}}{0.03696\,\frac{atm}{min}} = \left(\frac{0.44\ atm}{0.88\ atm}\right)^q \qquad \frac{1}{2} = \left(\frac{1}{2}\right)^q \qquad q = 1$$

b. Use one set of data from the table to calculate the value and unit of *k*. *Hint:* What unit must *k* have in order for the rate to have the unit atm/min?

$$0.01848\,\frac{atm}{min} = k(0.44atm) \qquad k = \frac{0.01848\,\frac{atm}{min}}{0.44\ atm} = 0.042\ min^{-1}$$

20. Consider the data below.

rate = $k[KI]^n$

[KI]	Initial Rate
0.10 M	8.4×10^{-6} M/s
0.30 M	7.6×10^{-5} M/s

a. Determine the order of the reaction with respect to potassium iodide. Justify your answer with an explanation or a mathematical equation.

When the concentration of KI triples, the initial rate increases by a factor of 9. Therefore the order of reaction with respect to KI is 2.

$$\frac{8.4\times 10^{-6}\,\frac{M}{s}}{7.6\times 10^{-5}\,\frac{M}{s}} = \left(\frac{0.10\ M}{0.30\ M}\right)^q \qquad \frac{1}{9} = \left(\frac{1}{3}\right)^q \qquad q = 2$$

b. Use one set of data from the table to calculate the value and unit of the rate constant *k*. *Hint:* The units of *k* in this question will not be the same units as the *k* in Question 19.

$$8.4 \times 10^{-6}\ m/s = k[0.10\ M]^2 \qquad k = \frac{8.4 \times 10^{-6}\ m/s}{[0.10\ M]^2} = 8.4 \times 10^{-4}\ m^{-1}/s^{-1}$$

$$k = \frac{0.01848\,\frac{atm}{min}}{0.44\ atm} = 0.042\ min^{-1}$$

21. Consider the data below.

rate = $k[H_2O_2]^n$

$[H_2O_2]$	Initial Rate
0.20 M	382 M/s
0.56 M	382 M/s

a. Determine the order of the reaction with respect to hydrogen peroxide. Justify your answer with an explanation or a mathematical equation.

When the concentration of H_2O_2 changes, the initial rate does not change. Therefore, the order of reaction with respect to H_2O_2 is zero.

$$\frac{382\frac{M}{s}}{382\frac{M}{s}} = \left(\frac{0.20\,M}{0.56\,M}\right)^q \qquad 1 = \left(\frac{0.2}{0.56}\right)^q \qquad q = 0$$

b. Use one set of data from the table to calculate the value and unit of the rate constant *k*.

$$382\frac{M}{s} = k(0.20\,M)^0 \qquad k = \frac{382\frac{M}{s}}{(0.20\,M)^0} = 382\,M \times s^{-1}$$

Read This!

The rate of a reaction is obtained by determining the concentration of a reactant or product in the reaction over time. This could occur through spectrophotometry for colored solutions, pressure changes for gaseous components, temperature changes for highly endothermic or exothermic reactions or pH for acids or bases—just to name a few. When concentration data are graphed versus time the slope of the curve is the rate of the reaction at that moment. Because the rate may change as the concentrations of reactants change the initial rate is the most dependable data point to use when determining the order of a reaction.

Model 3 – Reaction with Two Reactants

	$[N_2]$	$[H_2]$	Initial Rate
Trial 1	4.3×10^{-3} M	2.2×10^{-4} M	9.60×10^{-6} M/s
Trial 2	4.3×10^{-3} M	4.4×10^{-4} M	9.60×10^{-6} M/s
Trial 3	8.6×10^{-3} M	4.4×10^{-4} M	1.92×10^{-5} M/s

22. What are the reactants of the process being studied in Model 3?

The reactants in the process are nitrogen gas and hydrogen gas.

23. Consider the data in Model 3.

a. Compare the concentration of nitrogen in trials 1 and 2.

The concentrations of nitrogen in those trials are the same.

b. Compare the concentration of nitrogen in trials 1 and 3.

The concentration of nitrogen in trial 3 is double the concentration in trial 1.

Read This!

When there are multiple reactants in a process, each reactant must be studied independently while the other reactant is held at constant concentration. This allows the experimenter to determine the effect of changing the concentration of a specific reactant on the initial rate.

24. Consider the data in Model 3.

    a. Which trials should be considered when determining the order of reaction with respect to nitrogen gas?

    When determining the order of reaction with respect to nitrogen gas, the concentration of hydrogen gas must be controlled. Therefore, trials 2 and 3 should be considered.

    b. Which trials should be considered when determining the order of reaction with respect to hydrogen gas?

    When determining the order of reaction with respect to hydrogen gas, the concentration of nitrogen gas must be controlled. Therefore, trials 1 and 2 should be considered.

25. Explain why no useful conclusion about the exponents of the rate law could be drawn by comparing the data in trials 1 and 3 of Model 3.

    In trials 1 and 3, both concentrations have changed. Therefore, it is impossible to know if the change in rate is due to the change in nitrogen concentration or the change in hydrogen concentration.

26. Determine the order of reaction with respect to nitrogen.

    When the concentration of N_2 doubles (with the concentration of hydrogen being controlled), the initial rate doubles. Therefore, the order of reaction with respect to N_2 is first order.

$$\frac{9.60\times 10^{-6}\frac{M}{s}}{1.92\times 10^{-5}\frac{M}{s}} = \left(\frac{4.3\times 10^{-3}\,M}{8.6\times 10^{-3}\,M}\right)^{q}\left(\frac{4.4\times 10^{-4}\,M}{4.4\times 10^{-4}\,M}\right)^{p} \qquad \frac{1}{2} = \left(\frac{1}{2}\right)^{q}(1) \qquad q = 1$$

27. Determine the order of reaction with respect to hydrogen.

    When the concentration of H_2 doubles (with the concentration of nitrogen being controlled), the initial rate is unchanged. Therefore, the order of reaction with respect to H_2 is zero.

$$\frac{9.60\times 10^{-6}\frac{M}{s}}{9.60\times 10^{-6}\frac{M}{s}} = \left(\frac{4.3\times 10^{-3}\,M}{4.3\times 10^{-3}\,M}\right)^{q}\left(\frac{2.2\times 10^{-4}\,M}{4.4\times 10^{-4}\,M}\right)^{p} \qquad 1 = (1)\left(\frac{1}{2}\right)^{p} \qquad q = 0$$

28. Write the full rate law for the process in Model 3.

    Rate = $k[N_2]$

29. Use data from Model 3 to determine the value and unit of the rate constant, *k*, in the rate law.

$$9.60\times 10^{-6}\frac{M}{s} = k(4.3\times 10^{-3}M)^{1}(2.2\times 10^{-4}M)^{0}$$

$$k = \frac{9.60\times 10^{-6}\frac{M}{s}}{(4.3\times 10^{-3}M)^{1}(2.2\times 10^{-4}M)^{0}} = 2.2\times 10^{-3}s^{-1}$$

30. Use the data below to determine the rate law for the process shown. Include the value and units on the rate constant *k* in your answer.

$2NO(g) + O_2(g) \rightarrow NO_2(g)$

Experiment	Initial [NO] (mole L^{-1})	Initial [O_2] (mole L^{-1})	Initial Rate of Formation of NO_2 (mole $L^{-1}s^{-1}$)
1	0.10	0.10	2.5×10^{-4}
2	0.20	0.10	5.0×10^{-4}
3	0.20	0.40	8.0×10^{-3}

When the concentration of NO doubles (with the concentration of oxygen being controlled), the initial rate doubles. Therefore, the order of reaction with respect to NO is first order.

$$\frac{2.5\times 10^{-4}\frac{M}{s}}{5.0\times 10^{-4}\frac{M}{s}} = \left(\frac{0.10\,M}{0.20\,M}\right)^{q} = \left(\frac{0.10\,M}{0.10\,M}\right)^{p} \qquad \frac{1}{2} = \left(\frac{1}{2}\right)^{q} \qquad q = 1$$

When the concentration of O_2 quadruples (with the concentration of NO being controlled), the initial rate increases by 16. Therefore, the order of reaction with respect to O_2 is second order.

$$\frac{5.0\times 10^{-4}\frac{M}{s}}{8.0\times 10^{-3}\frac{M}{s}} = \left(\frac{0.20\,M}{0.20\,M}\right)^{q} = \left(\frac{0.10\,M}{0.40\,M}\right)^{p} \qquad \frac{1}{16} = (1)\left(\frac{1}{4}\right)^{q} \qquad q = 2$$

$$Rate = k[NO][O_2]^2$$

$$2.5\times 10^{-4}\frac{M}{s} = k(0.10\,M)(0.10\,M)^2$$

$$k = 0.25\frac{1}{M^2s}$$

29. Use data from Model 3 to determine the value and unit of the rate constant, *k*, in the rate law.

$$9.60 \times 10^{-6} \frac{M}{s} = \mathrm{k}(4.3 \times 10^{-3} M)^1(2.2 \times 10^{-4} M)^0$$

$$\mathrm{k} = \frac{9.60 \times 10^{-6} \frac{M}{s}}{(4.3 \times 10^{-3} M)^1(2.2 \times 10^{-4} M)^0} = 2.2 \times 10^{-3} s^{-1}$$

30. Use the data below to determine the rate law for the process shown. Include the value and units on the rate constant *k* in your answer.

$2NO(g) + O_2(g) \rightarrow NO_2(g)$

Experiment	**Initial [NO] (mole L^{-1})**	**Initial [O_2] (mole L^{-1})**	**Initial Rate of Formation of NO_2 (mole $L^{-1}s^{-1}$)**
1	0.10	0.10	2.5×10^{-4}
2	0.20	0.10	5.0×10^{-4}
3	0.20	0.40	8.0×10^{-3}

When the concentration of NO doubles (with the concentration of oxygen being controlled), the initial rate doubles. Therefore, the order of reaction with respect to NO is first order.

$$\frac{2.5 \times 10^{-4} \frac{M}{s}}{5.0 \times 10^{-4} \frac{M}{s}} = \left(\frac{0.10\,M}{0.20\,M}\right)^{q} = \left(\frac{0.10\,M}{0.10\,M}\right)^{p} \qquad \frac{1}{2} = \left(\frac{1}{2}\right)^{q} \qquad q = 1$$

When the concentration of O_2 quadruples (with the concentration of NO being controlled), the initial rate increases by 16. Therefore, the order of reaction with respect to O_2 is second order.

$$\frac{5.0 \times 10^{-4} \frac{M}{s}}{8.0 \times 10^{-3} \frac{M}{s}} = \left(\frac{0.20\,M}{0.20\,M}\right)^{q} = \left(\frac{0.10\,M}{0.40\,M}\right)^{p} \qquad \frac{1}{16} = (1)\left(\frac{1}{4}\right)^{q} \qquad q = 2$$

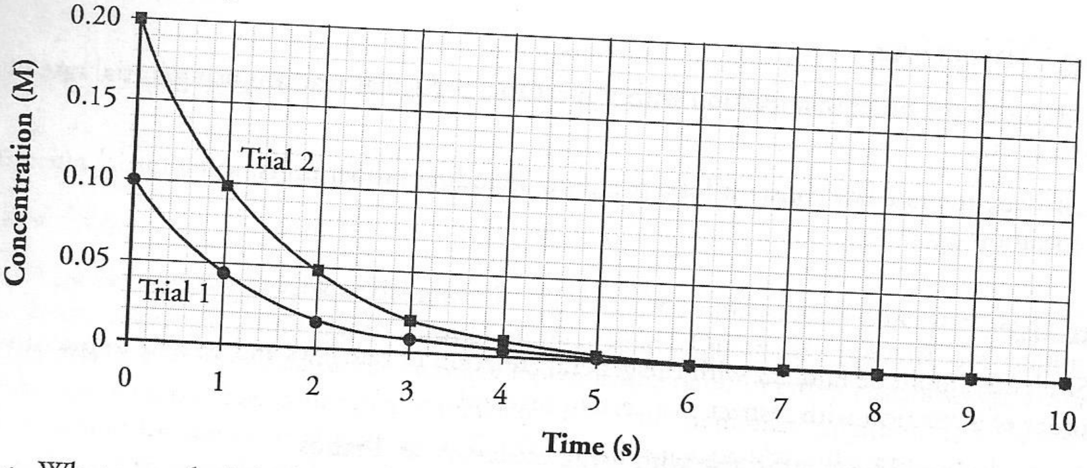
$$Rate = \mathrm{k}[NO][O_2]^2$$

$$2.5 \times 10^{-4} \frac{M}{s} = \mathrm{k}(0.10\,M)(0.10\,M)^2$$

$$\mathrm{k} = 0.25 \frac{1}{M^2 s}$$

Extension Questions

31. Consider the graph below.



a. What were the initial concentrations of the reactant being studied in the two trials for this rate law experiment?

The initial concentrations of the reactant were trial 1 = 0.10 M and trial 2 = 0.20 M.

b. Estimate the initial rate for each trial using data from the graph.

Trial 1 rate = 0.05 M/s
Trial 2 rate = 0.1 M/s
These values are found by taking slopes of the tangents to the curves.

c. Estimate the rate for each trial between 4 and 5 seconds into the reaction.

Trial 1 rate between 4 and 5 seconds = 0.01 M/s
Trial 2 rate at 4.5 seconds = 0.02 M/s

d. Why is the initial rate preferred to rates determined later in the process for determining the order of reaction with respect to a particular reactant?

The initial rates (slopes of a tangent to the curve) are very different between the two trials. The rates at the end of the reaction are very similar because they are nearly zero. This would make comparisons difficult.

Teacher Resources – Method of Initial Rates

Learning Objectives

1. Determine the order of a reaction with respect to a particular reactant using initial rate of reaction data.
2. Calculate the rate law constant for a reaction, including proper units, using initial rate and concentration data.

Prerequisites

1. Students should be familiar with the general equation of rate laws and be able to refer to the order of a reaction with respect to a certain reactant.
2. Students should be comfortable with using exponents and ratios.

Assessment Questions

1. If the change in concentration of a reactant has no effect on the initial rate of reaction, the order of reaction with respect to that reactant is

   a. 0.

   b. 1.

   c. 2.

   d. unknown.

2. If doubling the concentration of a reactant makes the initial rate of reaction double the order of reaction with respect to that reactant is

   a. 0.

   b. 1.

   c. 2.

   d. unknown.

3. Consider the data below. Determine the rate law for the reaction, including the value and units for the rate constant, *k*.

	$[O_2]$	$[SO_2]$	**Initial Rate**
Trial 1	2.4×10^{-3} M	3.7×10^{-4} M	4.30×10^{-3} M/s
Trial 2	2.4×10^{-3} M	7.4×10^{-4} M	1.72×10^{-2} M/s
Trial 3	4.8×10^{-3} M	7.4×10^{-4} M	3.44×10^{-2} M/s

Assessment Target Responses

1. *a*
2. *b*
3. $Rate = k[O_2][SO_2]^2$

   $k = 1.31 \times 10^7 M^{-2}s^{-1}$

Teacher Tips

- Students' abilities to look at the ratios in the data for an initial rates experiment vary. Some can do the calculations and reason through in their heads. Others struggle with determining the exponent that would cause the changes shown in the data. In either case however, students must be able to articulate, either in a sentence or with a mathematical equation, how they arrived at an exponent for the order of a reactant. For full credit on a problem like these on the AP exam, they will need to provide evidence for their answer.
- Lab data for initial rate experiments is often not pretty. Due to experimental error, the rates do not "double" or "quadruple" as they should. This is a good time to introduce the use of logarithms to solve for the exponent.

$$\frac{\text{Rate}_A}{\text{Rate}_B} = \frac{k[M]^x_A}{k[M]^x_B} \qquad \frac{\text{Rate}_A}{\text{Rate}_B} = \left(\frac{[M]_A}{[M]_B}\right)^x \qquad \frac{\log\left(\frac{\text{Rate}_A}{\text{Rate}_B}\right)}{\log\left(\frac{[M]_A}{[M]_B}\right)} = x$$

Alignment with AP Chemistry Framework

- **Essential Knowledge 4.A.2:** The rate law shows how the rate depends on reactant concentrations.

  Learning Objective 4.2 The student is able to analyze concentration versus time data to determine the rate law for a zeroth-, first-, or second-order reaction.

Free Energy

When will a reaction happen spontaneously?

Why?

Some reactions happen without us doing anything. Leave a piece of metal out in the weather, and you get rust. Lower the temperature of water below its freezing point, and it turns into ice. Other reactions need help. As you can imagine, it is important for chemists to understand which reactions are which. You would not want a reaction to spontaneously start when you were not ready for it to do so. Chemists need a way to predict the spontaneity of a reaction.

Model 1 – Spontaneous Processes

	Process Description	**Change in Enthalpy (ΔH)**	**Change in Entropy (ΔS)**	**Spontaneous?**
A	Two pure substances → Homogeneous mixture	~ 0	Increasing	Yes
B	Salt + Water → Salt water solution	~ 0	Increasing	Yes
C	$2H_2O_2$ (l) → $2H_2O$ (l) + O_2 (g)	Exothermic (negative)	Increasing (positive)	Yes
D	C_3H_8 (l) + $5O_2$ (g) → $3CO_2$ (g) + $4H_2O$ (g)	Exothermic	Increasing	Yes
E	$6CO_2$ (g) + $6H_2O$ (g) → $C_6H_{12}O_6$ (s) + $6O_2$ (g)	Endothermic	Decreasing	No
F	Glucose → Starch	Endothermic	Decreasing	No
G	Liquid water → Ice	Exothermic	Decreasing	Below 0 °C, Yes Above 0 °C, No
H	Cold water (25 °C) → Hot water (60 °C)	Endothermic	Increasing	Below 60 °C, No Above 60 °C, Yes

1. Consider Model 1.

   a. What two terms are used to describe the enthalpy changes for the reactions?

   Enthalpy changes are described as endothermic or exothermic.

   b. What is the symbol for the change in enthalpy?

   The symbol for the change in enthalpy is ΔH.

   c. What sign (+ or –) does the change in enthalpy have when the reaction releases heat energy to the surroundings?

   Energy is released to the surroundings when the process is exothermic. The ΔH in that case is negative.

2. Refer to Model 1. For each process below indicate if the change would be endothermic or exothermic.
   - *a.* A plant making glucose from carbon dioxide and water.

     Endothermic.
   - *b.* An ice cube melting.

     Endothermic.
   - *c.* Synthesis of hydrogen peroxide from water and oxygen.

     Endothermic.

3. According to Model 1, are all exothermic reactions spontaneous? If no, provide a counter example from Model 1.

STOP

No. Process G is exothermic, but only spontaneous under certain conditions.

4. Consider Model 1.
   - *a.* What is the symbol for the change in entropy of a system?

     The symbol for the change in entropy is ΔS.
   - *b.* When the entropy of a system increases, what sign (+ or –) is used?

     An increase in entropy is signified by a positive value.

5. According to Model 1, is there a relationship between the change in enthalpy and the change in entropy for a system or do they appear to be unrelated? If yes, describe the relationship.

   There is no relationship. There are examples in Model 1 of both endothermic and exothermic reactions that have an increase in entropy.

6. Refer to Model 1. For each process below, indicate if the entropy would increase or decrease.
   - *a.* Food coloring mixing into water.

     This is an increase in entropy.
   - *b.* A hot substance cooling to room temperature.

     This is a decrease in entropy.
   - *c.* The respiration of glucose and oxygen to produce carbon dioxide and water.

     This is an increase in entropy.

7. For each of the processes in Model 1, decide as a group if the molecules in the substances have more order (are more organized) before or after the reaction. Circle the side of the reaction with more order.

   See Model 1. Generally, solids are more ordered than liquids, and solutions are less ordered than the pure substances that form them.

8. Is there a correlation between the level of organization in the molecules and a change in entropy according to the examples in Model 1? Justify your reasoning.

STOP

Yes, there is a correlation between the level of organization in the molecules and the change in entropy. As the system becomes more disorganized and random, the entropy increases.

Read This!

The **entropy** of a system can be thought of as a measurement of the amount of disorder in the molecules that make up the system. The study of entropy is based in statistics. There are only a few ways in which a system can be organized and have low entropy, but there are usually many more ways in which a system can be disorganized and have high entropy. Therefore, systems are more likely to exist in higher entropy states. Think of your bedroom at home. If you do not spend energy to clean it, is it likely to be organized or disorganized?

9. Predict if the following processes would have an increase in entropy or a decrease in entropy based on what you have learned from Model 1.

   a. Water evaporating from a wet sidewalk.

   This would be an increase in entropy.

   b. Separating a mixture into pure substances.

   This would be a decrease in entropy.

   c. The cooling of molten metal.

   This would be a decrease in entropy.

   d. Decomposition of a compound into its elements.

   This would be an increase in entropy.

10. Is an increase in entropy of a system sufficient to make a process spontaneous? Justify your reasoning with evidence from Model 1.

    No. Process H in Model 1 has increasing entropy and is only spontaneous under certain conditions.

Read This!

Some of the processes in Model 1 are **spontaneous**—that is they will occur without any additional work being done on the system. For example, a solute will dissolve in water until it reaches saturation. However, glucose will not spontaneously form from carbon dioxide and water in the atmosphere. The **Second Law of Thermodynamics** states that a process will be spontaneous when it results in an increase of total entropy in the universe. In other words, either the system, the surroundings or both must have an increase in entropy. *Note:* the term "spontaneous" does not imply that the change will happen quickly. Rusting is spontaneous under the right conditions, but still occurs very slowly.

11. Consider the exothermic reactions in Model 1. When those reactions occur, what typically happens to the temperature of the surroundings?

    The energy released from the exothermic reaction typically increases the temperature of the surroundings.

12. Predict the change in entropy of the surroundings for an exothermic reaction.

    Because the temperature went up, the entropy of the surroundings increased. Increased temperatures cause atmospheric gas molecules to move in more random, disorganized ways.

13. Predict the change in entropy of the surroundings for an endothermic reaction.

    Because the temperature will go down, the entropy of the surroundings decreases, since atmospheric molecules will move at slower speeds.

STOP

14. Provide the letter of at least one process from Model 1 that illustrates each of the following conditions that will result in a spontaneous reaction.

  a. Both the system and surroundings have an increase in entropy.

  Processes C and D

  b. The increase in entropy of the system exceeds the decrease in entropy of the surroundings.

  Process H above 60 °C

  c. The increase in entropy of the surroundings exceeds the decrease in entropy of the system.

  Process G below 0 °C

Read This!

When a process is spontaneous, it can be used to do work. For example, we burn fuels via combustion to heat food or move vehicles. The amount of work that can be done by a spontaneous process is called **Gibbs free energy**, named after the mathematician who developed the concept in 1873. Josiah Willard Gibbs proposed this equation, which scientists use to calculate the free energy change for a process.

$$\Delta G = \Delta H - T\Delta S$$

When ΔG is negative, the process is spontaneous and can do work (**exergonic**). When ΔG is positive, the process is not spontaneous, and work must be done on the system to make it happen (**endergonic**).

15. Consider the signs (+ or –) on the enthalpy and entropy of process C in Model 1. Use the Gibbs free energy equation to explain why process C is a spontaneous reaction.

  In process C, the change in enthalpy is negative, and the change in entropy is positive.

  $\Delta G = \Delta H - T\Delta S$

  A negative number minus a positive number will always result in a negative number. Therefore, ΔG *will always be negative, and the reaction will be spontaneous.*

16. Consider the signs (+ or –) on the enthalpy and entropy of process E in Model 1. Use the Gibbs free energy equation to explain why process E is not a spontaneous reaction.

  In process E, the change in enthalpy is positive, and the change in entropy is negative.

  $\Delta G = \Delta H - T\Delta S$

  A positive number minus a negative number will always result in a positive number. Therefore, ΔG *will always be positive, and the reaction will never be spontaneous.*

17. Processes A and B in Model 1 have very minimal energy changes. Explain why those processes are spontaneous.

  In these processes, the change in enthalpy is near zero so the only factor that must be considered is the entropy of the system. Both processes have an increase in the entropy of the system, and therefore, ΔG *will be negative.*

18. Consider process G in Model 1.

    a. What is the entropy change for the system?

    Process G has a decrease in entropy.

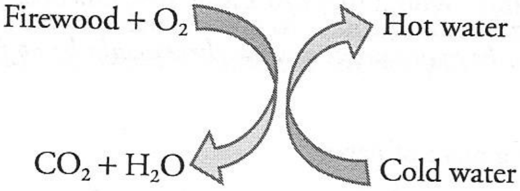
    b. What is the entropy change for the surroundings?

    The process is exothermic, so the entropy of the surroundings increases.

Read This!

We use **coupled processes** all the time to make things happen in life. In other words, a spontaneous reaction, which provides "free energy" and can do work, is used to make a nonspontaneous reaction happen. For example, your mobile device will not play music or light up spontaneously, but couple it with a battery containing a spontaneous chemical process and suddenly you can dance, text and play all afternoon.

19. If you have ever been camping, you may have used coupled processes to make yourself some hot cocoa in the evening.



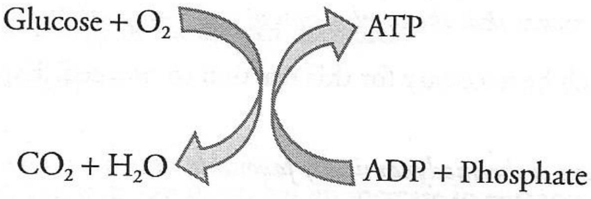
    a. Which of the processes above is exergonic, and does work?

    The burning of firewood is exergonic.

    b. Which of the processes above is endergonic, and has work done to it?

    The heating of water is endergonic.

20. Biological systems utilize coupled processes all the time to support life. Consider the coupled processes below.



    a. Which of the processes above is exergonic and does work?

    The respiration of glucose in the cells is exergonic.

    b. Which of the processes above is endergonic and has work done to it?

    The formation of ATP is endergonic.

Extension Questions

21. Are the terms exothermic and exergonic synonymous? Justify your answer with examples.

    No. The term exothermic only refers to the exchange of thermal energy between the system and the surroundings. The term exergonic refers to whether or not free energy is available from the process.

22. Life cannot exist in a completely closed system (no energy or matter comes into or out of the system).

    a. Explain why this is true based on the Second Law of Thermodynamics.

    For life to exist in a completely closed system, there must be more exergonic processes than endergonic processes. If energy was not available from outside the system, this could not be the case.

    b. The planet Earth is not a closed system. Ultimately, what is the source of all energy for life on Earth?

    Energy from the sun provides all life on Earth with free energy.

23. Consider a process where the increase in entropy of the system is exactly equal to the decrease in entropy of the surroundings. Would that process be spontaneous? Justify your reasoning.

    No, that process would not be spontaneous because there would be no free energy available to make the process happen.

24. Consider the burning of a piece of paper.

    a. Is the combustion of paper endothermic or exothermic?

    The combustion of paper is exothermic.

    b. Does the entropy of the system increase or decrease when paper burns? Explain your reasoning.

    The products of combustion are many more moles of gas, so the entropy would increase.

    c. Predict the sign of ΔG for the burning of paper. Is the combustion of paper spontaneous according to ΔG?

    The sign of ΔG *for the burning of paper should be negative because both the enthalpy and entropy are favorable. This means that the combustion of paper is spontaneous.*

    d. Why would a match be necessary for this reaction to proceed? Explain using thermodynamic terms.

    Although the reaction is thermodynamically favorable, it is not kinetically favorable. The rate is too slow because of a large activation energy requirement. The match is needed to overcome the activation energy requirement.

Teacher Resources – Free Energy

Learning Objectives

1. Relate the entropy of a system to the degree of organization of the molecules in the system.
2. Relate the change in energy for a process to the relative potential energy of the reactants and products in the process.
3. Describe the entropy and enthalpy changes that will make a process spontaneous.

Prerequisites

1. Students should be familiar with the terms enthalpy, exothermic and endothermic, and be able to describe the relative potential energies of the reactants and products in an exothermic reaction.
2. Students should be familiar with types of reactions such as decomposition, synthesis and combustion. It is also helpful if they have a general sense of which types of reactions tend to be exothermic or endothermic.
3. Students should have a basic understanding of photosynthesis and respiration, including the energy required or released, the overall chemical equations and the use of ATP as an energy carrier.

Assessment Questions

1. A process that releases heat energy to the surroundings is an ________ reaction, while a process that can do work is an ____________ reaction.
   a. endothermic / endergonic
   b. exothermic / exergonic
   c. endergonic / endothermic
   d. exergonic / exothermic
2. A process will be spontaneous when
   a. the total potential energy of the system decreases.
   b. the reaction is exothermic.
   c. the system has an increase in entropy.
   d. the universe (system + surroundings) has an increase in entropy.
3. Provide an example of humans using coupled reactions to create order.

Assessment Target Responses

1. *b*
2. *d*
3. *Answers may vary. Students should describe an exergonic process coupled with an endergonic process. Examples include use of electricity (from a power plant) to manufacture goods or refrigeration to freeze water.*

Teacher Tip

- Gibbs free energy is a difficult concept for students to understand because enthalpy, entropy and temperature are all factors that contribute to a process being spontaneous or not. Actual numeric values for these three variables were purposely avoided in this activity in the hopes that conceptual understanding rather than algorithmic understanding would be the result.

Alignment with AP Chemistry Framework

- **Essential Knowledge 5.E.1:** Entropy is a measure of the dispersal of matter and energy.

  Learning Objective 5.12 The student is able to use representations and models to predict the sign and relative magnitude of the entropy change associated with chemical or physical processes.

- **Essential Knowledge 5.E.2:** Some physical or chemical processes involved both a decrease in the internal energy of the components ($\Delta H° < 0$) under consideration and an increase in the entropy of those components ($\Delta S° > 0$). These processes are necessarily "thermodynamically favored" ($\Delta G° < 0$).

  Learning Objective 5.13 The student is able to predict whether or not a physical or chemical process is thermodynamically favored by determination of (either quantitatively or qualitatively) the signs of both $\Delta H°$ and $\Delta S°$, and calculation or estimation of $\Delta G°$ when needed.

- **Essential knowledge 5.E.3:** If a chemical or physical process is not driven by both entropy and enthalpy changes, then the Gibbs free energy change can be used to determine whether the process is thermodynamically favored.

  Learning Objective 5.14 The student is able to determine whether a chemical or physical process is thermodynamically favorable by calculating the change in standard Gibbs energy.

- **Essential knowledge 5.E.4:** External sources of energy can be used to drive change in cases where the Gibbs free energy change is positive.

  Learning Objective 5.15 The student is able to explain how the application of external energy sources or the coupling of favorable with unfavorable reactions can be used to cause processes that are not thermodynamically favorable to become favorable.

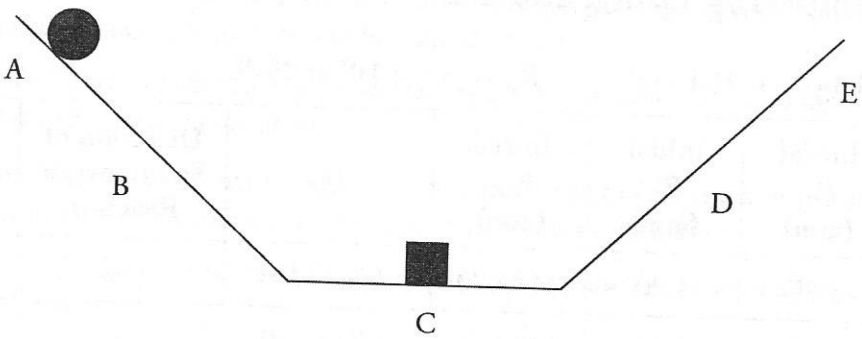
Work, Equilibrium and Free Energy

Does the work done by a reaction change with different amounts of reactants?

Why?

The scientific definition of work is force acting on an object to move it some distance. If the object does not move, then no work was done. The farther it moves, the more work was done. Chemical reactions can be used to do work. A reaction might produce a gas that could move a piston or produce an electrical current that could run a motor. Gibbs free energy, ΔG, is equal to the work that can be done by ($\Delta G<0$) or must be done on ($\Delta G>0$) a reaction. The amount of work is dependent on how many moles of substance must react before reaching equilibrium.

Model 1 – Moving a Block



1. Consider the ramp system in Model 1. The block at position C is a freely moving, frictionless object.
   a. When the ball is released from position A where will it go?

   The ball will roll to position C and hit the block.

   b. When the ball hits the block at the bottom of the ramp what will happen?

   The block will move to the right.

2. Compare what will happen to the block when the ball is released from position A to what will happen when the ball is released from position B. Explain your reasoning.

   When the ball is released from position A, it will move the block with greater acceleration than if the ball is released at position B. The ball at position A has more potential energy.

3. Is more work done by the ball when it is released from position A or position B? Explain your reasoning.

   More work is done by the ball on the block when it is released from position A, because the ball will move the block farther when it is released from position A.

4. Compare what will happen to the block when the ball is released from position A to what will happen when the ball is released from position E. Explain your reasoning.

   The block will move with the same acceleration, but in the opposite direction. Position A and position E are equal heights from the block, so the amount of potential energy the ball will have in those positions is equal. However, the direction the block will move is different.

5. Is more work done by the ball when it is released from position A or position E?

   The amounts of work done by the ball will be equal.

6. Identify two other positions on the ramp system that the ball could be released from and do an equal amount of work, but in opposite directions.

   Positions B and D will result in equal work, but move the block in opposite directions.

7. How much work will be done by the ball if it is released from a position just to the left or right of position C? Explain your reasoning.

   The ball will do no work if it is released from a position near position C because it will not move or hit the block. Its potential energy is zero.

STOP

Model 2 – Comparing Q, K_{eq} and ΔG

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ $K_p = 6.0 \times 10^5$ at 25 °C

Trial	Initial P_{N_2} (atm)	Initial P_{H_2} (atm)	Initial P_{NH_3} (atm)	Q_P	Direction of Spontaneous Reaction	$\Delta G \rightarrow$ (J)
1	3.85	1.20	1499.70	3.38×10^5	→	−1420
2	3.83	1.16	1499.76	3.76×10^5	→	−1150
3	3.81	1.12	1499.82	4.20×10^5	→	−879
4	3.79	1.08	1499.88	4.71×10^5	→	−595
5	3.77	1.04	1499.94	5.31×10^5	→	−302
6	3.75	1.00	1500.00	6.00×10^5	←→	0
7	3.73	0.96	1500.06	6.82×10^5	←	320
8	3.71	0.92	1500.12	7.79×10^5	←	650
9	3.69	0.88	1500.18	8.95×10^5	←	994
10	3.67	0.84	1500.24	10.3×10^5	←	1350

8. Write the equilibrium constant expression, K_p, for the reaction in Model 2.

$$K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$$

9. Based on the value of K_p, does this reaction favor products or reactants?

   The K_p is very large, so the reaction favors products.

10. For each of the 10 trials of the reaction in Model 2, calculate the reaction quotient, Q_p. Divide the work among group members.

    See Model 2.

11. According to the calculated Q_p values, were any of the trials at equilibrium initially? Justify your reasoning.

    Yes, the Q_p *of trial six was equal to the* K_p, *so that trial was at equilibrium initially.*

12. Compare the Q_p and K_p for each trial and indicate with an arrow the direction the reaction will need to go to reach equilibrium.

    See Model 2.

13. Consider the ΔG values provided in Model 2.

    a. List the trials in which work will be done by the system (the reaction would be spontaneous) when the reaction proceeds in the forward direction.

    Trials 1–5 have negative ΔG *values so those reactions would be able to do work when the reaction proceeds in the forward direction.*

    b. List the trials in which work must be done to the system (the reaction would not be spontaneous) in order for the reaction to proceed in the forward direction.

    Trials 7–10 have positive ΔG *values so those reactions would need work done to them in order to proceed forward.*

    c. For the trials just listed in part *b*, would work need to be done on the system (nonspontaneous), or would work be done by the system (spontaneous) when the reaction proceeded in the **reverse** direction?

    If trials 7–10 reacted in the reverse direction, work would be done by the system because the sign on ΔG *would reverse and be negative.*

14. Circle the correct word to complete the sentence based on the data in Model 2.

    a. When a reaction spontaneously proceeds toward equilibrium in the ([✓ forward]/reverse) direction, ΔG is a negative number ($\Delta G < 0$).

    b. When a reaction spontaneously proceeds toward equilibrium in the (forward/[✓ reverse]) direction, ΔG is a positive number ($\Delta G > 0$).

15. What is the value of ΔG when a reaction is at equilibrium and will spontaneously react in both directions?

    When the reaction is at equilibrium, the ΔG *is equal to zero.*

16. According to the data in Model 2, if the reaction is already at equilibrium, how much work can be done by the reaction?

    No work is done by the reaction if it is already in equilibrium.

17. Compare the Q_p values for trials 1 and 4 in Model 2.

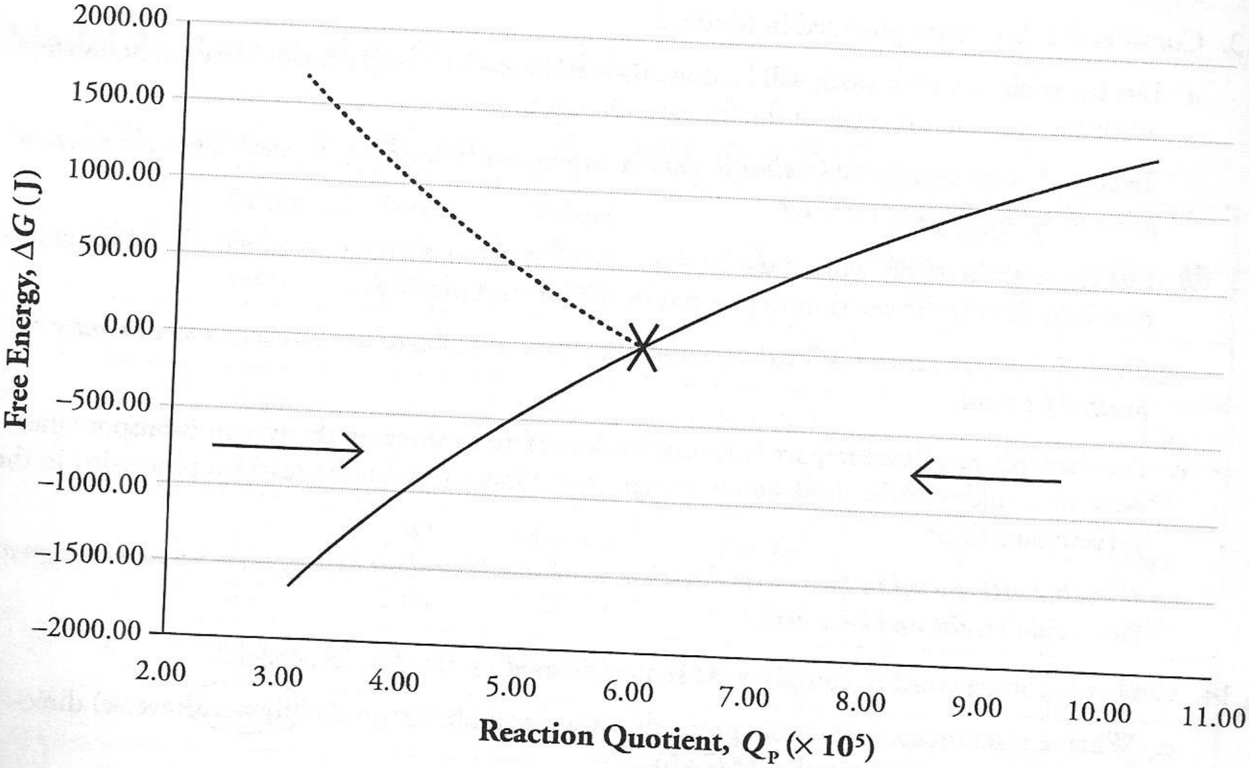
   a. In which trial must more moles of nitrogen react in order to reach equilibrium?

   More moles of nitrogen will need to react in trial 1 because the Q_p value is further from the K_p value than the Q_p value for trial 4.

   b. In which trial will the reaction do more work as it proceeds towards equilibrium? Justify your answer.

   Trial 1 will do more work because the ΔG for that trial is larger.

Model 3 – Graph of ΔG versus Q_p



18. Mark an "X" on the line in the graph to indicate the point at which the system from Model 2 is at equilibrium.

   See Model 3.

19. Consider the points that are to the left of the "X." In which direction would the reaction proceed spontaneously for these points? Add an arrow to Model 3 to show the direction.

   See Model 3. These points represent Q_p values less that K_p, so the reactions would proceed spontaneously in the forward direction.

20. Consider the points that are to the right of the "X." In which direction would the reaction proceed spontaneously for these points? Add an arrow to Model 3 to show the direction.

   See Model 3. These points represent Q_p values greater than K_p, so the reactions would proceed spontaneously in the reverse direction.

21. The sign of ΔG has nothing to do with the amount of work that is done, but rather is the direction the reaction will proceed spontaneously. Now that we have arrows on the graph to indicate direction, let's just look at the value of ΔG. Sketch a line representing the absolute value of ΔG versus Q_p.

    See Model 3.

22. Imagine the ball from Model 1 is placed on the absolute value graph in Model 3.

    a. If the ball started at $Q_p = 9.0 \times 10^5$, which direction would it roll?

    The ball would roll to the left.

    b. At what point on the absolute value graph would the ball eventually come to rest?

    The ball would stop at $\Delta G = 0$*, or on the X.*

    c. If the ball started at $Q_p = 3.0 \times 10^5$, which direction would it roll?

    The ball would roll to the right.

    d. At what point on the absolute value graph would the ball eventually come to rest?

    The ball would stop at $\Delta G = 0$*, or on the X.*

23. Imagine the ball from Model 1 is rolling along the graph in Model 3.

    a. How does the work done by the ball compare when it starts at $Q_p = 3.0 \times 10^5$ and when it starts at $Q_p = 5.0 \times 10^5$?

    The ball would be able to do more work if it was released from $Q_p = 3.0 \times 10^5$*.*

    b. How does the work done by the ball compare when $Q_p = 9.0 \times 10^5$ to when $Q_p = 4.0 \times 10^5$?

    The ball would do the same amount of work if released from these two positions, but the direction of the reaction would be different. When the ball is at $Q_p = 9.0 \times 10^5$*, the reaction must go in the reverse direction for work to be done by the system. But when the ball is at* $Q_p = 4.0 \times 10^5$*, work is done by the system in the forward direction.*

STOP

24. Imagine you start the reaction in Model 2 with the conditions of trial 4 and you want to end the reaction with the conditions of trial 1.

    a. Would work be done by the system or would work need to be done on the system to make this change? Justify your reasoning.

    Because the system would be moving away from the equilibrium state, work would need to be done on the system.

    b. How much work would be done or required to make this change?

    This would require 825 J of work.

25. In complete sentences, discuss how a ball on a ramp system like that in Model 1 could be an analogy for reactions proceeding from various starting conditions toward equilibrium. You may want to include diagrams with your answer.

    The ball on the ramp system is a good analogy for a chemical reaction proceeding toward equilibrium. The ball can move either to the right or left. A chemical reaction can move either in the forward (right) or reverse (left) directions. In both cases, they will only move (or react) until they reach the lowest potential energy state—equilibrium.

    When the ball is higher from the bottom of the ramp system, it is able to do more work. When a chemical reaction starts further from its equilibrium state, it is able to do more work as it reacts.

    The ball only does work when it rolls down the ramp system toward the lowest point. For the ball to move to a higher point, work must be done on the ball. In a chemical reaction, work is done as the reaction proceeds to equilibrium (from either direction). For a reaction to react in either direction and move further from equilibrium, work will need to be done on the system.

26. List the conditions required for $\Delta G°$.

    All gases must be at a partial pressure of 1.000 atmosphere.

    All solutions must have a molarity of 1.000 M.

    The temperature must be 25°C.

27. Are any of the ΔG's in Model 2 equal to $\Delta G°$? Justify your reasoning.

    No, none of the ΔG values in Model 2 are equal to $\Delta G°$. The standard state free energy, signified by the degree sign after the symbol, indicates all partial pressures of gases are at 1.00 atm. This is not the case in any of the trials in Model 2.

28. Would the $\Delta G°$ for the reaction in Model 2 be positive or negative? Justify your reasoning.

    The standard state free energy is the free energy when all partial pressures are equal to 1 atmosphere. Therefore, the Q_p would be equal to 1. This is far smaller than any of the Q_p values in Model 2. Following the trend shown in Model 2, the $\Delta G°$ would be a large negative number.

Extension Questions

29. A student in class states “A reaction can never proceed past equilibrium.” Use the concepts from this activity to support the student’s statement.

    A reaction will always move spontaneously toward equilibrium, but once there, it would take work to move back out of equilibrium. The change in free energy is always negative when a reaction is moving toward equilibrium.

30. Look at the reaction in Model 2.

    a. Based on the change in moles of gas, predict the sign on the entropy term, ΔS.

    The reaction goes from four moles of gas down to two. This would indicate an increase in order, making ΔS *a negative value.*

    b. Is the reaction exothermic or endothermic? Justify your reasoning.

    Since the reaction has a negative ΔG *value in the forward direction, the* ΔH *must be favorable. Therefore, the reaction must be exothermic.*

    c. The reaction system can do work when it proceeds in the forward direction. Based on the information in this activity, which of the methods listed below is the most likely method by which the work is done? Support your answer with an explanation.

    - Expansion of a gas.
    - Electrical current.
    - Heating a substance.

    Since the reaction actually has a reduction in the number of moles, the work cannot be done with the expansion of a gas. The reaction is also not a redox reaction that might be used to produce an electrical current, so the work cannot be done with electricity. The reaction is, however, exothermic. Therefore, the work must be done as the heating of the surroundings.

Teacher Resources – Work, Equilibrium and Free Energy

Learning Objectives

1. Predict the sign of ΔG when given the initial conditions of a reaction and the K_{eq} or K_p.
2. Compare the amount of work that will be done by or would need to be done on a system given two sets of initial conditions for a given reaction.

Prerequisites

1. Students should understand how the sign on the free energy relates to the spontaneous direction of a reaction and how that relates to the work that can be done by a reaction or the work that must be done on a reaction.
2. Students must know the conditions required for standard state Gibbs free energy, $\Delta G°$.
3. Students should be able to calculate the equilibrium constant, K_p of a reaction involving all gaseous substances.
4. Students should be able to predict the direction of a reaction by calculating the reaction quotient, Q_P and compare it to the equilibrium constant K_p.
5. Students should be able to calculate the absolute value of a number.

Assessment Questions

1. Which of the following statements is false?
   a. The ΔG for a reaction heading toward equilibrium is always negative.
   b. The ΔG for a reaction at equilibrium is always zero.
   c. The $\Delta G°$ for a reaction is equal to zero when the reaction is at equilibrium.
   d. A reaction cannot move out of equilibrium spontaneously.
2. Fifty milliliters of 1.00×10^{-3} M sodium chloride is added to 100.0 mL of 1.00×10^{-6} M silver nitrate solution. Compare the Q_{sp} to the K_{sp} to determine if work will be done by the system in this situation? The K_{sp} for silver chloride is 1.8×10^{-10}.
3. Consider the two sets of initial conditions below for the given chemical process. Which trial will do more work as the reaction proceeds towards equilibrium?

$CH_3COOH\,(aq) + NH_3\,(aq) \leftrightarrow CH_3COO^{1-}\,(aq) + NH_4^{1+}\,(aq) \quad K_{eq} = 3.0 \times 10^4$

	Trial A	Trial B
$[CH_3COOH]$	1.00 M	0.50 M
$[NH_3]$	1.00 M	0.75 M
$[CH_3COO^{1-}]$	0.005 M	0.005 M
$[NH_4^{1+}]$	0.005 M	0.005 M

Target Responses – Assessment Questions

1. *c*
2. *Yes, for this situation* $Q_{sp} = 2.22 \times 10^{-10}$*, so a precipitate will form spontaneously.*
3. *Trial A.*

Teacher Tips

- This activity is a qualitative treatment of work, equilibrium and free energy. The traditional treatment of this topic with equations such as

  $$\Delta G = \Delta G^\circ + RT\,ln\,Q \text{ and } \Delta G^\circ = -RT\,ln\,K$$

  would best be done after this activity is completed.
- One of the most difficult concepts related to free energy is the difference between ΔG and ΔG°. This activity will help to show that ΔG° is simply one of the many ΔG's that could be calculated for a reaction at various starting conditions. The sign of ΔG° depends on whether the standard conditions give a reaction quotient, Q_{eq}, larger or smaller than K_{eq}.
- In Question 23, some students will justify their answers based on the length of the travel path of the ball rather than the height the ball must fall to get to equilibrium. Make sure to point out that it is only the magnitude of the change in y that gives the work done.

Alignment with AP Chemistry Framework

- **Essential Knowledge 6.A.3:** When a system is at equilibrium, all macroscopic variables, such as concentrations, partial pressures, and temperature, do not change over time. Equilibrium results from an equality between the rates of the forward and reverse reactions, at which point $Q = K$.

  Learning Objective 6.4 The student can, given a set of intial conditions (concentrations or partial pressures) and the equilibrium constant, K, use the tendency of Q to approach K to predict and justify the prediction as to whether the reaction will proceed toward products or reactants as equilibrium is approached.

Reaction Quotient

How do you predict which direction a reaction will proceed to reach equilibrium?

Why?

When a reaction reaches equilibrium there must be some non-negligible amount of every species in the reaction, otherwise the reaction cannot react in both directions. Knowing this, it is very easy to predict which direction a reaction will go to reach equilibrium when one of the components of the reaction has an initial concentration of zero. Many of the problems you have worked with thus far have some component at zero concentration, but real life does not work that way. Most of the time, the reaction in question has some measureable amount of every species. Deciding which way the reaction will go to reach equilibrium then becomes more challenging.

Model 1 – A Theoretical Equilibrium

Trial 1	$A(g) + B(g) \leftrightarrow C(g)$		
Initial	1.000 M	1.000 M	1.000 M
Change	⟵		
Equilibrium	1.464 M	1.464 M	0.536 M

Trial 2	$A(g) + B(g) \leftrightarrow C(g)$		
Initial	2.000 M	0.500 M	0.500 M
Change	<----------		
Equilibrium	2.150 M	0.650 M	0.350 M

Trial 3	$A(g) + B(g) \leftrightarrow C(g)$		
Initial	1.000 M	0.500 M	1.500 M
Change	<----------		
Equilibrium	1.864 M	1.364 M	0.636 M

Trial 4	$A(g) + B(g) \leftrightarrow C(g)$		
Initial	1.600 M	1.000 M	0.400 M
Change	*No change*		
Equilibrium	1.600 M	1.000 M	0.400 M

Trial 5	$A(g) + B(g) \leftrightarrow C(g)$		
Initial	1.400 M	1.200 M	0.400 M
Change	---------->		
Equilibrium	1.388 M	1.188 M	0.412 M

Trial 6	$A(g) + B(g) \leftrightarrow C(g)$		
Initial	0.750 M	2.000 M	0.250 M
Change	---------->		
Equilibrium	0.675 M	1.925 M	0.325 M

1. Examine Model 1.
   a. Write the theoretical chemical reaction that is used in the trials of Model 1.

   $A(g) + B(g) \leftrightarrow C(g)$

   b. If 0.50 M of reactant A reacts, predict the change in concentration of B and C.

   Since all of the coefficients in the reaction are one, the concentration of B will decrease by 0.50 M and the concentration of C will increase by 0.50 M.

2. What variables were changed in the different trials shown in Model 1?

   Each trial in Model 1 has different initial concentrations of the three species.

3. In Trial 1 of Model 1 there is an arrow in the "change" section of the table.

   a. Explain what that arrow represents.

   The arrow indicates the direction that the reaction shifts in order to reach equilibrium.

   b. What evidence is present in the table to indicate the direction the arrow should be pointing?

   The concentration of the product, C, decreased and the concentrations of the reactants, A and B, increased. That indicates the reaction shifted in the reverse direction.

4. With your group, determine which direction each of the other trials in Model 1 reacted to reach equilibrium. Indicate that direction with an arrow in the "change" section of the table.

   See Model 1.

5. Is it true that there are equal concentrations of reactants and products when all of the reactions in Model 1 reach equilibrium? Justify your answer with evidence from Model 1.

   No. Even if the reactant concentrations are added together, they do not equal the product concentrations in any of the trials.

6. According to Model 1, are the final concentrations of all species in the reaction the same when the reaction reaches equilibrium, regardless of the initial concentration?

   No, each of the trials in Model 1 has a different equilibrium concentration.

7. Does the reaction in Model 1 always proceed in the forward direction when there are more reactants than products? Justify your answer with evidence from Model 1.

   No. In Trial 2 of Model 1, there are far more reactants than products, and the reaction went in the reverse direction.

STOP

8. Write the equilibrium constant expression for the reaction in Model 1.

$$K_{eq} = \frac{[C]}{[A][B]}$$

9. Discuss with your group how you could determine the equilibrium constant, K_{eq}, for the reaction in Model 1. Divide the work among group members. Use data from multiple trials to calculate the equilibrium constant for the reaction and determine the average. Show all work.

   The equilibrium data from each trial in Model 1 can be used to calculate the equilibrium constant.

Trial 1

$$K_{eq} = \frac{(0.536\ M)}{(1.464\ M)(1.464\ M)}$$

$$K_{eq} = 0.250$$

Trial 2

$$K_{eq} = \frac{(0.350\ M)}{(2.150\ M)(0.650\ M)}$$

$$K_{eq} = 0.250$$

Trial 3

$$K_{eq} = \frac{(0.636\ M)}{(1.864\ M)(1.364\ M)}$$

$$K_{eq} = 0.250$$

Average = *0.250*

Read This!

The key to knowing which direction a reaction will need to proceed in order to reach equilibrium is knowing if you have too much reactant or too much product compared to the equilibrium state. Keep in mind, however, that there are many combinations of reactant and product concentrations that constitute an equilibrium state.

Model 2 – Comparing Q and K_{eq}

Trial	Reaction Quotient, Q	Equilibrium Constant, K_{eq}	Q versus K_{eq}	Direction to Equilibrium
1	*1.000*	*0.250*	$>$	←
2	*0.500*	*0.250*	$>$	←
3	*3.00*	*0.250*	$>$	←
4	*0.250*	*0.250*	$=$	*No change*
5	*0.238*	*0.250*	$<$	→
6	*0.167*	*0.250*	$<$	→

10. Fill in the Equilibrium Constant column in Model 2 using data from Model 1.
    See Model 2.

11. Fill in the Direction to Equilibrium column in Model 2 using data from Model 1.
    See Model 2.

Read This!

The **reaction quotient** for a reaction is the ratio of products to reactants, similar to the equilibrium constant. The difference is you calculate the ratio with initial conditions.

$$K_{eq} = \frac{[C]_{eq}}{[A]_{eq}[B]_{eq}} \qquad Q = \frac{[C]_{initial}}{[A]_{initial}[B]_{initial}}$$

12. Calculate the reaction quotient for each of the trials in Model 1 and record the data in Model 2 in the appropriate column. Divide the work among group members. Show your work below.

Trial 1

$$Q = \frac{(1.000\ M)}{(1.000\ M)(1.000\ M)}$$

$Q = 1.000$

Trial 2

$$Q = \frac{(0.500\ M)}{(2.000\ M)(0.500\ M)}$$

$Q = 0.500$

Trial 3

$$Q = \frac{(1.500\ M)}{(1.000\ M)(0.500\ M)}$$

$Q = 3.000$

13. Consider how the concentration values in the reaction quotient change when the reaction proceeds in the forward direction.

    a. Does the numerator increase or decrease?

    The numerator represents the products. In a forward reaction, the products increase. Therefore, the numerator of Q will increase as the reaction proceeds in the forward direction.

    b. Does the denominator increase or decrease?

    The denominator represents the reactants. In a forward reaction, the reactants decrease. Therefore, the denominator of Q will decrease as the reaction proceeds in the forward direction.

    c. Overall, does the Q ratio increase or decrease when the reaction proceeds in the forward direction?

    The numerator increases and the denominator decreases, so Q will increase overall.

14. Consider how the concentration values in the reaction quotient change when the reaction proceeds in the reverse direction.

    a. Does the numerator increase or decrease?

    The numerator represents the products. In a reverse reaction, the products decrease. Therefore, the numerator of Q will decrease as the reaction proceeds in the reverse direction.

    b. Does the denominator increase or decrease?

    The denominator represents the reactants. In a reverse reaction, the reactants increase. Therefore, the denominator of Q will increase as the reaction proceeds in the reverse direction.

    c. Overall does the Q ratio increase or decrease when the reaction proceeds in the forward direction?

    The numerator decreases and the denominator increases, so Q will decrease overall.

15. Fill in the Q versus K_{eq} column in the table in Model 2. Write $Q > K_{eq}$, $Q < K_{eq}$ or $Q = K_{eq}$.

    See Model 2.

16. Complete the following statements.

    a. When the reaction quotient is **greater than** the equilibrium constant, the reaction proceeds more in (the forward, [✓ the reverse,] neither) direction to reach equilibrium.

    b. When the reaction quotient is **less than** the equilibrium constant, the reaction proceeds more in ([✓ the forward,] the reverse, neither) direction to reach equilibrium.

    c. When the reaction quotient is **equal to** the equilibrium constant, the reaction proceeds more in (the forward, the reverse, [✓ neither]) direction to reach equilibrium.

17. Consider the following reaction.

$$2SO_2(g) + O_2(g) \longleftrightarrow 2SO_3(g) \qquad K_{eq} = 3900 \text{ at } 2000\text{ K}$$

a. Write the equilibrium constant expression for the reaction.

$$K_{eq} = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

b. Write the reaction quotient expression for the reaction.

$$Q = \frac{[SO_3]^2_{initial}}{[SO_2]^2_{initial}[O_2]_{initial}}$$

c. A reaction vessel contains 0.150 M sulfur dioxide, 0.150 M oxygen and 2.000 M sulfur trioxide. Predict the direction the reaction must shift to reach equilibrium. Show a calculation to justify your answer.

$$Q = \frac{(2.000\ M)^2}{(0.150\ M)^2(0.150\ M)} = 1185$$

Since Q is less than K$_{eq}$, the reaction will shift forward to reach equilibrium.

18. Consider the following reaction.

$$2HI(g) \longleftrightarrow H_2(g) + I_2(g) \qquad K_{eq} = 0.25 \text{ at } 25\,°C$$

A reaction vessel contains 0.500 M hydrogen, 0.500 M iodine vapor and 0.750 M hydrogen iodide. Predict the direction the reaction must shift to react equilibrium. Show a calculation to justify your answer.

$$Q = \frac{[H_2]_{initial}[I_2]_{initial}}{[HI]^2_{initial}}$$

$$Q = \frac{(0.500\ M)(0.500\ M)}{(0.750\ M)^2} = 0.444$$

Since Q is greater than K$_{eq}$, the reaction will shift in the reverse direction to reach equilibrium.

Extension Questions

19. Consider the following reaction.

$$Cd^{2+}(aq) + 4Cl^{1-}(aq) \longleftrightarrow CdCl_4^{2-}(aq) \qquad K_{eq} = 108 \text{ at } 25\,°C$$

a. Write the reaction quotient expression for the reaction.

$$Q = \frac{[CdCl_4^{2-}]_i}{[Cd^{2+}]_i[Cl^{1-}]_i}$$

where i = initial.

b. A reaction vessel contains 0.100 M cadmium ion, 0.500 M chloride and 0.250 M tetrachlorocadmate ion. Predict the direction the reaction must shift to reach equilibrium. Show a calculation to justify your answer.

$$Q = \frac{(0.250\ M)}{(0.100\ M)(0.500\ M)^4} = 40$$

Since Q is less than K_{eq}, the reaction would shift in the forward direction to reach equilibrium.

20. Consider the following reaction.

$$C(s) + H_2O(g) \longleftrightarrow H_2(g) + CO(g) \qquad K_{eq} = 4.09 \times 10^{-3} \text{ at } 2000\ K$$

a. A 1.000-L reaction vessel contains 4.00 M of water vapor, 0.040 M hydrogen and 0.040 M carbon monoxide. Calculate the reaction quotient and state which direction the quotient predicts the reaction must shift to reach equilibrium.

$$Q = \frac{[H_2]_i[CO]_i}{[H_2O]_i}$$

$$Q = \frac{(0.040\ M)(0.040\ M)}{4.00\ M} = 4.00 \times 10^{-3}$$

Based on the Q value, the reaction would need to proceed in the forward direction to reach equilibrium because Q is less than K_{eq}.

b. Discuss why the prediction above is wrong in this case.

According to the initial conditions stated in the problem, there is no carbon solid present in the reaction vessel. Therefore, the reaction must react in the reverse direction to reach equilibrium. The reaction quotient does not take solids into account and therefore cannot predict the direction of this equilibrium.

21. LeChâtelier's principle states that an equilibrium system will shift in the direction that reduces the stress put on the system. Is this consistent with the predictions made by calculating the reaction quotient and comparing *Q* to the equilibrium constant? Provide an example to support your answer.

Yes. Suppose that a system at equilibrium has some extra reactant added to the reaction vessel. LeChâtelier predicts the reaction will move in the forward direction to reduce the added substance. The added reactant will also increase the value of the denominator of Q, making it lower than K_{eq} for the reaction. This would also result in a prediction of a forward reaction to reach equilibrium. Therefore, the two methods of predicting the direction a reaction shifts are consistent.

Teacher Resources – Reaction Quotient

Learning Objectives

1. Write the reaction quotient, Q, for a chemical equilibrium.
2. Calculate the reaction quotient ratio using initial concentrations of all gaseous species in a chemical equilibrium.
3. Predict the direction in which the reaction will appear to proceed to reach equilibrium by comparing the reaction quotient to the equilibrium constant, K_{eq}.

Prerequisites

1. Students should be able to write an equilibrium constant expression for a chemical equilibrium.
2. Students should understand that reversible reactions react in both directions until equilibrium is reached. The equilibrium state may be different for different trials if the initial conditions differ.

Assessment Questions

1. Write the reaction quotient expression for the following chemical equilibrium.

$$N_2(g) + 3Cl_2(g) \longleftrightarrow 2NCl_3(g)$$

2. Which of the following is true for a reaction where the reaction quotient, Q, is greater than the equilibrium constant, K_{eq}?
   a. The reaction reacts only in the forward direction.
   b. The reaction reacts only in the reverse direction.
   c. The reaction reacts in both directions, but faster in the forward direction.
   d. The reaction reacts in both directions, but faster in the reverse direction.
3. Consider the following equilibrium. The equilibrium constant for this reaction is 0.030 at 250 °C. Predict which direction the reaction will shift in order to reach equilibrium if the reaction vessel initially contains 0.100 M PCl_5, 0.500 M PCl_3 and 0.010 M Cl_2.

$$PCl_5(g) \longleftrightarrow PCl_3(g) + Cl_2(g)$$

Assessment Target Responses

1. $Q = \dfrac{[NCl_3]_i^2}{[N_2]_i[Cl_2]_i^3}$
2. *d*
3. $Q > K_{eq}$, *therefore the reaction will shift in the reverse direction.*

Teacher Tips

- Throughout this activity be mindful of how students are talking about the chemical equilibria systems. It is very easy for students to say the reaction "reacts forward" or "reacts backward," but do they realize that the equilibrium systems are always reacting in BOTH directions? Ask students to articulate this understanding at least once during the activity and then agree upon common language that you find acceptable. Should the students talk about how the reaction "shifts," or do you prefer they say the reaction reacts faster in one direction compared to the other?
- Using a visual model or simulation to illustrate how a reaction reaches equilibrium from a variety of initial states can be very helpful to students.
- The main portion of this activity uses only gas phase equilibria examples. Depending on when you approach this topic in your study of equilibrium systems, you may or may not want to use the extension questions that use heterogeneous equilibria examples. If students are not aware of how to deal with pure solids or liquids in an equilibrium system, you may want to avoid the extension questions.

Alignment with AP Chemistry Framework

- **Essential knowledge 6.A.2:** The current state of a system undergoing a reversible reaction can be characterized by the extent to which reactants have been converted to products. The relative quantities of reaction components are quantitatively described by the reaction quotient, Q.
- **Essential knowledge 6.A.3:** When a system is at equilibrium, all macroscopic variables, such as concentrations, partial pressures and temperature, do not change over time. Equilibrium results from an equality between the rates of the forward and reverse reactions, at which point $Q = K$.

  Learning Objective 6.4 The student can, given a set of initial conditions (concentrations or partial pressures) and the equilibrium constant, K, use the tendency of Q to approach K to predict and justify the prediction as to whether the reaction will proceed toward products or reactants as equilibrium is approached.

Common Ion Effect on Solubility

How is the solubility of a solid affected by other ion species in solution?

Why?

The solubility product (K_{sp}) for a salt allows chemists to predict the concentration of dissolved ions in solution. At this point you have learned to calculate the concentration of ions in water when an insoluble salt is dissolved in pure water. But what if the beaker already has some ions dissolved in it? Can the salt still dissolve to the same extent? Is the solubility of the salt changed?

Model 1 – Dissolving a Salt in 500 mL of Solution

Note: Proceed to Question 1. Do not fill in these tables until instructed to do so.

$$Ca(OH)_2(s) \leftrightarrow Ca^{2+}(aq) + 2OH^{1-}(aq) \quad K_{sp} = 5.5 \times 10^{-6}$$

Beaker 1

	Ca^{2+}	OH^{1-}
Initial	0 M	0 M
Change	$+x$	$+2x$
Equilibrium	x	$2x$

$K_{sp} = [Ca^{2+}][OH^{1-}]^2$

$5.5 \times 10^{-6} = (x)(2x)^2$

$5.5 \times 10^{-6} = 4x^3$

$x = 0.11\ M$

Beaker 2

	Ca^{2+}	OH^{1-}
Initial	0 M	0.200 M
Change	$+x$	$+2x$
Equilibrium	x	$0.200 + 2x$

$K_{sp} = [Ca^{2+}][OH^{1-}]^2$

$5.5 \times 10^{-6} = (x)(0.200 + 2x)^2$

$5.5 \times 10^{-6} \approx 0.400x$

$x = 1.4 \times 10^{-4}\ M$

Beaker 3

	Ca^{2+}	OH^{1-}
Initial	0.200 M	0 M
Change	$+x$	$+2x$
Equilibrium	$0.200 + x$	$2x$

$K_{sp} = [Ca^{2+}][OH^{1-}]^2$

$5.5 \times 10^{-6} = (0.200 + 2x)(2x)^2$

$5.5 \times 10^{-6} \approx 0.200(2x)^2$

$x = 2.6 \times 10^{-3}\ M$

Beaker 4

	Ca^{2+}	OH^{1-}
Initial	0 M	0.500 M
Change	$+x$	$+2x$
Equilibrium	x	$0.500 + 2x$

$K_{sp} = [Ca^{2+}][OH^{1-}]^2$

$5.5 \times 10^{-6} = (x)(0.500 + 2x)^2$

$5.5 \times 10^{-6} = 0.500x$

$x = 1.1 \times 10^{-5}\ M$

1. The solubility of what salt is being investigated in the four beakers in Model 1?

   $Ca(OH)_2$

2. Why does solid $Ca(OH)_2$ not appear in the ICE tables in Model 1?

   Solid $Ca(OH)_2$ does not appear in the ICE tables in Model 1 because solids have constant concentrations owing to constant densities, and therefore do not appear in equilibrium constant expressions such as K_{sp}.

3. Match each of the following descriptions with one of the beakers in Model 1. In each case, assume the change in volume as the solid(s) are added is minimal.

   a. A 1.00 mole sample of solid calcium hydroxide is added to 500.0 mL of water in beaker *1*.

   b. A 1.00 mole sample of solid calcium hydroxide is added to 500.0 mL of 0.500 M sodium hydroxide solution in beaker *4*.

   c. A 1.00 mole sample of solid calcium hydroxide is added to 500.0 mL of 0.200 M sodium hydroxide solution in beaker *2*.

   d. A 1.00 mole sample of solid calcium hydroxide is added to 500.0 mL of 0.200 M calcium nitrate solution in beaker *3*.

4. Based on the solubility product constant, K_{sp}, for calcium hydroxide given in Model 1, do you expect most of the 1.00 mole sample of solid to dissolve in any of the four beakers?

   No, the solubility product constant, K_{sp} *for calcium hydroxide is very small, so only a small amount will dissolve in any of the beakers.*

5. Three of the beakers in Model 1 contain a **common ion** in solution.

   a. Which beakers in Model 1 contain a common ion?

   Beakers 2–4 contain a common ion.

   b. Consider the source of the common ion in each beaker. Does the common ion come from the insoluble salt? If no, explain the source of the common ion.

   No, the common ion does not come from the insoluble salt. The common ion comes from a different soluble salt that has one ion that matches one of the ions in the insoluble salt.

6. Predict what will be in Beakers 1 and 2 when the systems in those beakers reach equilibrium. Use particulate drawings below to communicate your predictions. You may omit water molecules for clarity.

   The exact ratio of dissolved to solid calcium hydroxide formula units is not critical since the students have not done any calculations at this point. What is important is that they show the majority of calcium hydroxide in the solid state, the ratio of calcium ions to hydroxide ions is 1:2 in Beaker 1, and much less than 1:2 in Beaker 2. It is important that they show an increased number of hydroxide ions in Beaker 2 compared to Beaker 1.

7. Write the equation for the solubility product constant, K_{sp}, for this salt.

   $K_{sp} = [Ca^{2+}][OH^{1-}]^2$

8. Divide the work among group members to fill in each of the ICE tables in Model 1. Use the solubility product constant to find the increase in Ca^{2+} ion concentration, or x value, in each beaker. Add this to Model 1. (Work space for these calculations has been provided in Model 1.)

   See Model 1.

9. What does a large *x* value mean? That is, do large *x* values mean more solid has dissolved?

   The larger the x *value, the more* Ca^{2+} *ions are dissolved in solution, or the more solid* $Ca(OH)_2$ *has dissolved.*

10. Does the presence of a common ion increase or decrease the solubility of the insoluble salt? Support your answer with evidence from Model 1.

    The presence of a common ion decreases the solubility of the insoluble salt. Beaker 1 does not contain a common ion. The change in concentration of calcium ion to reach equilibrium is 0.11 M. The rest of the beakers contain a common ion. The change in concentration of calcium ion to reach equilibrium is less than 0.11 M in all those beakers.

11. According to Model 1, as the concentration of the common ion is increased, how does the solubility of the insoluble salt change? Support your answer with evidence from Model 1.

    Beaker 2 has a common ion at 0.200 M while Beaker 4 has the same common ion at 0.500 M. The solubility of the calcium hydroxide is less in Beaker 4 than in Beaker 2. Therefore, as the concentration of the common ion is increased, the solubility of the insoluble salt decreases.

12. Are the data in Model 1 consistent with LeChâtelier's Principle? Support your answer with specific examples from Model 1.

    According to LeChâtelier's Principle, as the concentration of an equilibrium species increases, the reaction should shift in a direction that uses up that species. In Model 1, as the concentration of the common ion increases, the salt is less soluble (the reaction shifts left). This is consistent with LeChâtelier's Principle.

13. Consider the four beakers below. One-gram samples of barium sulfate, $BaSO_4$, are added to each beaker. Rank the beakers in terms of solubility of the barium sulfate from least soluble to most soluble. The solubility product constant for barium sulfate is $K_{sp} = 1.1 \times 10^{-10}$.

Beaker 1	**Beaker 2**	**Beaker 3**	**Beaker 4**
Water	0.100 M NaCl	0.100 M Na_2SO_4	0.200 M $Ba(NO_3)_2$

The salt would be least soluble in Beaker 4 as this beaker has the highest common ion concentration. Beaker 3 would have the next lowest solubility as it also contains a common ion. Beakers 1 and 2 would tie for the highest solubility. Although Beaker 2 contains other ions, neither of them are common ions, so there would be no effect on the solubility of the barium sulfate.

14. The solubility product constant, K_{sp}, for silver carbonate, Ag_2CO_3, is 8.10×10^{-12}. Compare the solubility of silver carbonate in water to its solubility in a 0.100 M solution of silver nitrate. Support your comparison with calculations similar to those in Model 1.

$Ag_2CO_3(s) \leftrightarrow 2Ag^{1+}(aq) + CO_3^{2-}(aq)$

Solubility of Ag_2CO_3 in water:

	Ag^{1+}	CO_3^{2-}
Initial	0 M	0 M
Change	+2x	+x
Equilibrium	2x	x

$K_{sp} = [Ag^{1+}]^2[CO_3^{2-}]$

$8.10 \times 10^{-12} = (2x)^2(x)$

$8.10 \times 10^{-12} = 4x^3$

$x = 1.27 \times 10^{-4}$ M

Solubility of Ag_2CO_3 in 0.100 M silver nitrate:

	Ag^{1+}	CO_3^{2-}
Initial	0.100 M	0 M
Change	+2x	+x
Equilibrium	0.100 + 2x	x

$K_{sp} = [Ag^{1+}]^2[CO_3^{2-}]$

$8.10 \times 10^{-12} = (0.100 + 2x)^2(x)$

$8.10 \times 10^{-12} \approx 0.0100x$

$x \approx 8.10 \times 10^{-10}$ M

The presence of the common ion (Ag^{1+}) decreases the solubility of Ag_2CO_3 and less $Ag^{2+}(aq)$ ions are given to the solution by the solid.

Extension Questions

15. In a precipitation reaction (otherwise known as a double replacement or metathesis reaction) the extent to which a precipitate is formed is dependent on the solubility product constant of the precipitate. A species with a large K_{sp} (highly soluble) may not precipitate until very high concentrations are reached. A species with a low K_{sp} (mostly insoluble) will precipitate readily. Use the ideas explored in this activity to explain why the formation of a precipitate may increase when non-stoichiometric amounts of reactants are used (one reactant will limit, while the other will be in excess).

    When the reactants in the double replacement reaction are not in a stoichiometric ratio, there will be a reactant in excess. This excess reactant will contain a common ion that will help to decrease the solubility of the precipitate. Thus, more precipitate will form.

16. Would the four beakers in Model 1 have the same reading on a pH meter? Explain your reasoning.

    No, they would not have the same reading. Each one contains a different concentration of hydroxide ions.

17. Consider any of the beakers in Model 1. Predict what might happen to the solubility of the insoluble salt if a 1.0 M acid solution was added dropwise to the beaker. *Hint:* Which ion species in the beaker will react with the acid? How will this reaction alter the concentration of the common ion?)

    The acid would react with the hydroxide ions, OH^{1-}, in solution. This would lower the concentration of the common ion. According to LeChâtelier's Principle, when the concentration of a species in the reaction decreases, the reaction will shift to produce more of that species. Therefore, the solubility of the insoluble salt will be increased as the reaction shifts right to make more hydroxide ions.

Teacher Resources – Common Ion Effect on Solubility

Learning Objectives

1. Describe the effect of a common ion in solution on the solubility of an insoluble salt.
2. Apply LeChâtelier's Principle and the common ion effect to either increase the formation of a precipitate or increase the solubility of a salt.

Prerequisites

1. Students should be able to use ICE tables to calculate the equilibrium concentrations of species in an equilibrium reaction.
2. Students should be comfortable with LeChâtelier's Principle and predicting the shift in a reaction when species concentrations are increased or decreased.
3. Students should have a basic understanding of neutralization reactions.

Assessment Questions

1. When a common ion is present in solution with an insoluble salt, the solubility of the insoluble salt is

   a. increased.

   b. decreased.

   c. unchanged.

   d. difficult to predict.

2. Which of the scenarios below describes an insoluble salt in the presence of a common ion?

   a. A beaker contains 100 mL of 0.100 M sodium nitrate and solid sodium chloride.

   b. A beaker contains 100 mL of 0.100 M silver nitrate and solid silver chloride.

   c. A beaker contains 100 mL of 0.100 M sodium nitrate and solid calcium carbonate.

   d. A beaker contains 100 mL of 0.100 M nitric acid and solid calcium hydroxide.

3. The solubility product constant, K_{sp}, for barium sulfate, $BaSO_4$, is 1.1×10^{-10}. Compare the solubility of barium sulfate in water to its solubility in a 0.100 M solution of sodium sulfate. Support your comparison with calculations.

Assessment Target Responses

1. *b*
2. *b*

3. *Solubility of $BaSO_4$ in water:*

	Ba^{2+}	SO_4^{2-}
Initial	*0 M*	*0 M*
Change	$+x$	$+x$
Equilibrium	x	x

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$
$$1.1 \times 10^{-10} = (x)(x)$$
$$1.1 \times 10^{-10} = x^2$$
$$x = 1.05 \times 10^{-5}\ M$$

Solubility of $BaSO_4$ in 0.100 M sodium sulfate:

	Ba^{2+}	SO_4^{2-}
Initial	*0 M*	*0.100 M*
Change	$+x$	$+x$
Equilibrium	x	$0.100 + x$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$
$$1.1 \times 10^{-10} = (x)(0.100 + x)$$
$$1.1 \times 10^{-10} \approx 0.100x$$
$$x \approx 1.1 \times 10^{-9}\ M$$

Teacher Tip

- This activity assumes students are skilled at solving K_{sp} equations to find the ion species in a solubility problem.

Alignment with AP Chemistry Framework

- **Essential Knowledge 6.C.3:** The solubility of a substance can be understood in terms of chemical equilibrium.

  Learning Objective 6.23 The student can interpret data regarding the relative solubility of salts in terms of factors (common ion, pH) that influence the solubility.

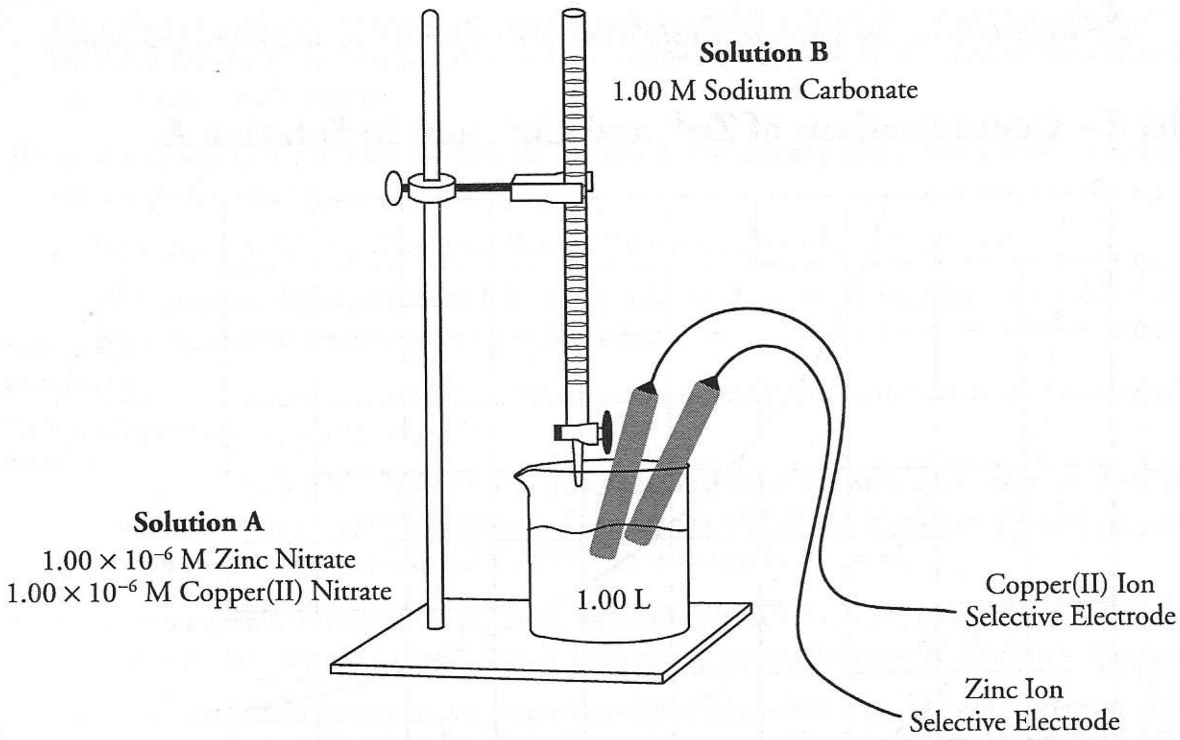
Fractional Precipitation

Can one type of cation be removed from an aqueous mixture of multiple cations by precipitation?

Why?

In both industry and research there are often times when one particular component of a mixture needs to be separated from a solution. Maybe it is a rare metal that is dissolved in a mixture of minerals. Maybe it is a particular protein from lysed plant cells. If the desired component is volatile, distillation could be used. But if the goal is to separate ions in solution, fractional precipitation is preferred.

Model 1 – A Precipitation Experiment


Solution B
1.00 M Sodium Carbonate
Solution A
1.00 × 10⁻⁶ M Zinc Nitrate
1.00 × 10⁻⁶ M Copper(II) Nitrate
1.00 L
Copper(II) Ion Selective Electrode
Zinc Ion Selective Electrode

1. Consider the experiment setup in Model 1.
   a. What cations and anions are present in solution A?

      Solution A contains Zn^{2+}, Cu^{2+} and NO_3^{1-}.

   b. What is the starting molar concentration of solution A for both zinc and copper(II) ions?

      1.00×10^{-6} M

   c. Identify the cations and anions present in solution B.

      Solution B contains Na^{1+} and CO_3^{2-} ions.

   d. What is the concentration of carbonate ions in solution B?

      1.00 M

2. When solution A and solution B mix, there is potential for two precipitates to form. Write double replacement reactions to show the formation of the two precipitates.

$Zn(NO_3)_2(aq) + Na_2CO_3(aq) \rightarrow ZnCO_3(s) + 2NaNO_3(aq)$

$Cu(NO_3)_2(aq) + Na_2CO_3(aq) \rightarrow CuCO_3(s) + 2NaNO_3(aq)$

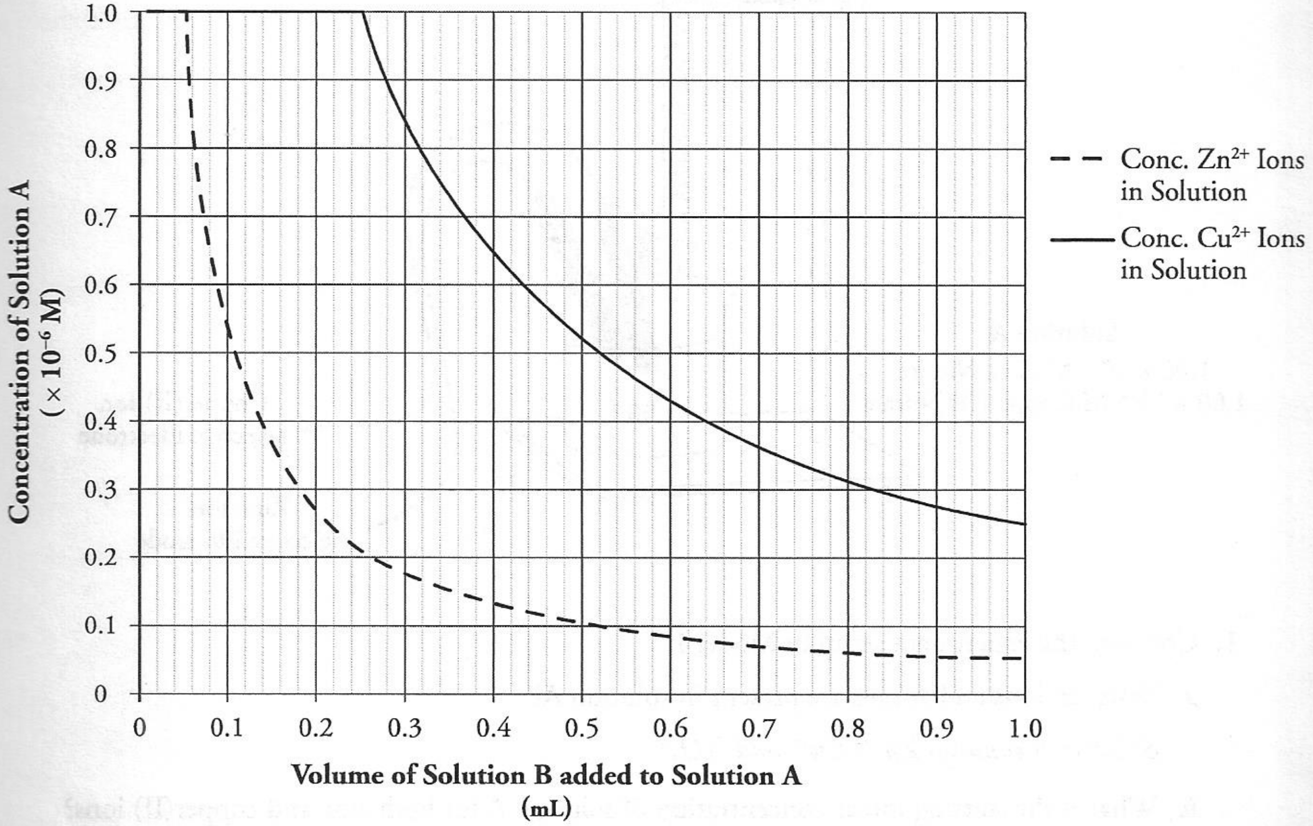
3. In the experiment setup in Model 1, how will the concentration of zinc and copper(II) ions in solution A be recorded during the experiment?

Ion selective electrodes are used to monitor the concentration of zinc and copper(II) ions during the experiment.

4. If solution B is added dropwise to solution A, eventually a precipitate will begin to form. What do you expect to happen to the concentration of either zinc or copper(II) ions in the solution?

As precipitate forms, the concentration of the zinc and copper(II) ions in solution will decrease.

Model 2 – Concentrations of Zn^{2+} and Cu^{2+} Ions in Solution A



5. Consider the graph in Model 2 that was produced by the experiment in Model 1 as solution B was added dropwise to solution A. Which line in the graph represents the concentration of zinc ions?

The dotted line represents the concentration of zinc ions.

6. Initially there is no change in the concentration of either metal cation in solution A. Explain why this is the case.

   The concentration of carbonate ions has not reached a sufficient level to cause precipitation. The solution is not saturated yet in either zinc or copper(II) carbonate.

7. According to the graph in Model 2, which precipitate is formed first during the experiment in Model 1—zinc carbonate or copper(II) carbonate? Justify your reasoning.

   Zinc carbonate is formed first because the dotted line shows a drop in zinc ion concentration with the addition of solution B earlier in the experiment than a drop in copper(II) ion concentration.

8. Which solute has the higher solubility—zinc carbonate or copper(II) carbonate? Justify your reasoning.

   Since the zinc carbonate precipitated with the addition of less solution B, it must have the lower solubility. Copper(II) carbonate continues to be soluble until a much higher concentration of carbonate ions is reached in the beaker.

9. Suppose a researcher wanted to "pull out" as much zinc ion as possible from solution A without any copper(II) impurity.

   a. How many milliliters of solution B should the researcher add to solution A?

   The researcher should add about 0.25 mL of solution B. At this point, addition of solution A begins to cause precipitation of copper(II) carbonate.

   b. What is the maximum percent of the original zinc ion that could be removed from solution A without any copper(II) impurity?

   This amount of solution B (0.25 mL) will precipitate out about 80% of the zinc ions from the solution without a copper(II) impurity. The addition of 0.25 mL of solution B lowers the concentration of Zn^{2+} *ions to about* 0.2×10^{-6} *M, as indicated by the graph.*

10. Suppose a researcher wanted to "pull out" as much copper(II) ion as possible from solution A without any zinc impurity. Could this be achieved by adding solution B? Explain your reasoning.

    No, carbonate cannot be used to precipitate out copper(II) without zinc. The zinc carbonate will always precipitate out first, based on the information presented in the graph in Model 2.

11. The solubility product constants for the two precipitates that formed when solution A and solution B are mixed are 5.4×10^{-11} and 2.5×10^{-10} at 25 °C. Assign these K_{sp} values to the two precipitates based on their relative solubilities.

    K_{sp} *for* $CuCO_3$ *is* 2.5×10^{-10}

    K_{sp} *for* $ZnCO_3$ *is* 5.4×10^{-11}

12. Write the Q_{sp} and K_{sp} expressions for both zinc carbonate and copper(II) carbonate in solution. Be sure to indicate when initial concentrations are being used in the equation and when equilibrium concentrations are being used in the equation.

For zinc carbonate:	*For copper(II) carbonate:*
$Q_{sp} = [Zn^{2+}]_{initial}[CO_3^{2-}]_{initial}$	$Q_{sp} = [Cu^{2+}]_{initial}[CO_3^{2-}]_{initial}$
$K_{sp} = [Zn^{2+}]_{eq}[CO_3^{2-}]_{eq}$	$K_{sp} = [Cu^{2+}]_{eq}[CO_3^{2-}]_{eq}$

Model 3 – Comparing Q_{sp} and K_{sp}

Volume of Solution B Added (mL)	$[CO_3^{2-}]$ Initial (M)	$[Zn^{2+}]$ Initial (M)	$ZnCO_3$ ppt? (Yes/No)	$ZnCO_3$ Reaction Quotient	$[Cu^{2+}]$ Initial (M)	$CuCO_3$ ppt? (Yes/No)	$CuCO_3$ Reaction Quotient
0.05	*0.00005*	1.00×10^{-6}	*No*	5.0×10^{-11}	1.00×10^{-6}	*No*	5.0×10^{-11}
0.10	*0.00010*	1.00×10^{-6}	*Yes*	1.0×10^{-10}	1.00×10^{-6}	*No*	1.0×10^{-10}
0.15	*0.00015*	1.00×10^{-6}	*Yes*	1.5×10^{-10}	1.00×10^{-6}	*No*	1.5×10^{-10}
0.20	*0.00020*	1.00×10^{-6}	*Yes*	2.0×10^{-10}	1.00×10^{-6}	*No*	2.0×10^{-10}
0.25	*0.00025*	1.00×10^{-6}	*Yes*	2.5×10^{-10}	1.00×10^{-6}	*No*	2.5×10^{-10}
0.30	*0.00030*	1.00×10^{-6}	*Yes*	3.0×10^{-10}	1.00×10^{-6}	*Yes*	3.0×10^{-10}
0.35	*0.00035*	1.00×10^{-6}	*Yes*	3.5×10^{-10}	1.00×10^{-6}	*Yes*	3.5×10^{-10}
0.40	*0.00040*	1.00×10^{-6}	*Yes*	4.0×10^{-10}	1.00×10^{-6}	*Yes*	4.0×10^{-10}

13. Calculate the initial concentration (before precipitation) of carbonate ions after the addition of each 0.05 mL of solution B to the 1.00 L beaker of solution A. Divide the work among group members and write the answers in the table in Model 3. Assume the volume change as solution B is added is negligible.

    See Model 3. Example calculation:

$$0.05\ mL\ of\ Solution\ B \times \frac{1\ L}{1000\ mL} = 0.00005\ L\ Solution\ B$$

$$0.00005\ L\ Solution\ B \times \frac{1\ mole\ B}{1\ L\ Solution} = \frac{0.00005\ moles}{1\ L} = 0.00005\ M$$

14. Notice the initial concentrations of Zn^{2+} and Cu^{2+} in the table in Model 3.

    a. Explain how these were obtained from the data in Model 2.

    The concentrations of these ions are taken from the first point on the graph's y-axis (before any sodium carbonate is added).

    b. As solution B is added and precipitates form, do these initial concentrations change?

    No, the initial concentrations, for calculation purposes, are always considered as that before precipitation.

15. Use the data in Model 2 to indicate the presence of precipitate (either $ZnCO_3$ or $CuCO_3$) after each 0.05 mL addition of solution B in Model 3.

    See Model 3. The presence of precipitate is confirmed by the drop in concentrations of Zn^{2+} and Cu^{2+}. These concentrations decrease because Zn^{2+} and Cu^{2+} are precipitated out of the solution.

16. Use the initial concentrations of carbonate ions and zinc ions to calculate the reaction quotient, Q_{sp}, for the zinc carbonate scenarios in Model 3. Divide the work among group members and write the answers in the table in Model 3.

    See Model 3.

    Example: $Q_{sp} = [Zn^{2+}][CO_3^{2-}] - [1.00 \times 10^{-6}][0.00005] = 5.0 \times 10^{-11}$

17. Use the initial concentrations of carbonate ion and copper(II) ions to calculate the reaction quotient, Q_{sp}, for the copper(II) carbonate scenarios in Model 3. Divide the work among group members and write the answers in the table in Model 3.

    See Model 3.

    Example: $Q_{sp} = [Cu^{2+}][CO_3^{2-}] = [1.00 \times 10^{-6}][0.00005] = 5.0 \times 10^{-11}$

18. Refer to Question 11 for the K_{sp} value for zinc carbonate and copper(II) carbonate. When a precipitate forms in solution, how do Q_{sp} and K_{sp} compare? Use data from Model 3 to support your answer.

    STOP

    A precipitate forms when Q_{sp} is larger than K_{sp}. When Q_{sp} is smaller than K_{sp}, no precipitate forms. When $Q_{sp} = K_{sp}$, the solution is saturated.

19. Consider the point at which zinc carbonate just begins to precipitate in Model 2.

    a. Use the K_{sp} for zinc carbonate to calculate the concentration of carbonate ions required in the 1.00-L beaker of solution A for a precipitate to form.

    $K_{sp} = [Zn^{2+}][CO_3^{2-}]$

    $5.4 \times 10^{-11} = (1.00 \times 10^{-6}\ M)\ [CO_3^{2-}]$

    $[CO_3^{2-}] = 5.4 \times 10^{-5}\ M$

    b. Calculate the volume of solution B that would need to be added to solution A to achieve the carbonate concentration calculated in part *a*.

    $(5.4 \times 10^{-5}\ M)(1000\ mL) = (1.00\ M)(x)$

    $x = 0.054\ mL$

    c. Is your answer in part *b* consistent with the graph in Model 2?

    Yes, this volume is consistent with the graph in Model 2. The solution A zinc ion concentration begins to drop, a signal of its precipitation from solution, as about 0.05 mL of solution B added.

20. Consider the point in the experiment when 0.20 mL of solution B has been added to solution A.
    a. Calculate the concentration of carbonate ions in the 1.00-L beaker of solution A at this point. Consider the volume of solution B negligible.

       $(0.20\ mL)(1.00\ M) = [CO_3^{2-}](1000\ mL)$

       $[CO_3^{2-}] = 2.0 \times 10^{-4}\ M$

    b. Use the K_{sp} of zinc carbonate to calculate the concentration of Zn^{2+} ions remaining in solution at this point.

       $K_{sp} = [Zn^{2+}][CO_3^{2-}]$

       $5.4 \times 10^{-11} = [Zn^{2+}](2.0 \times 10^{-4}\ M)$

       $[Zn^{2+}] = 2.7 \times 10^{-7}\ M = 0.27\ \mu M$

    c. Is your answer in part *b* consistent with the graph in Model 2?

       Yes, as 0.20 mL of solution B is added, the concentration of zinc ions remaining in solution is about 0.27 μM.

21. Use the K_{sp} for copper(II) carbonate to calculate the volume of solution B that must be added to solution A to cause a precipitate. Check your answer against the graph in Model 2. *Note:* Look back at Question 19 for steps on how to solve this question.

    $K_{sp} = [Cu^{2+}][CO_3^{2-}]$

    $2.5 \times 10^{-10} = (1.00 \times 10^{-6}\ M)[CO_3^{2-}]$

    $[CO_3^{2-}] = 2.5 \times 10^{-4}\ M$

    $(2.5 \times 10^{-4}\ M)(1000\ mL) = (1.00\ M)(x)$

    $x = 0.25\ mL$, *this value is close to that indicated on the graph.*

22. Use the K_{sp} of zinc carbonate to calculate the concentration of Zn^{2+} ions remaining in solution when copper(II) carbonate begins precipitating. Check your answer against the graph in Model 2. *Hint:* Look back at Question 20 for steps on how to solve this question.

    $K_{sp} = [Zn^{2+}][CO_3^{2-}]$

    $5.4 \times 10^{-11} = [Zn^{2+}](2.5 \times 10^{-4}\ M)$

    $[Zn^{2+}] = 2.2 \times 10^{-7}\ M = 0.22\ \mu M$, *this value is close to that indicated on the graph.*

STOP

23. A solution of 2.00 M sodium sulfide is added drop-wise to a solution that is 2.50×10^{-7} M in both cobalt(II) ion and nickel(II) ion. The K_{sp} of cobalt(II) sulfide and nickel(II) sulfide are 5.9×10^{-21} and 3.0×10^{-21}, respectively, at 25 °C.

a. Which precipitate will form first when the sodium sulfide is added? Explain your reasoning.

Nickel sulfide has a smaller K_{sp}*, so it is less soluble. It will precipitate first.*

b. What concentration of sodium sulfide will be required for the first precipitate to form?

$K_{sp} = [Ni^{2+}][S^{2-}]$

$3.0 \times 10^{-21} = (2.50 \times 10^{-7}\ M)[S^{2-}]$

$[S^{2-}] = 1.2 \times 10^{-14}\ M$

c. What concentration of sodium sulfide will be required for the second precipitate to form?

$K_{sp} = [Co^{2+}][S^{2-}]$

$5.9 \times 10^{-21} = (2.50 \times 10^{-7}\ M)[S^{2-}]$

$[S^{2-}] = 2.4 \times 10^{-14}\ M$

d. When the second precipitate begins to form, what is the concentration of metal ions that remains unprecipitated from the first precipitate?

$K_{sp} = [Ni^{2+}][S^{2-}]$

$3.0 \times 10^{-21} = [Ni^{2+}](2.4 \times 10^{-14}\ M)$

$[Ni^{2+}] = 1.3 \times 10^{-7}\ M$

Extension Questions

24. A 1.00 M solution of lead(II) nitrate is added drop-wise to 1.00 L of 0.0025 M sodium iodide and 0.0025 M sodium fluoride. The K_{sp} values of lead(II) iodide and lead(II) fluoride are 8.7×10^{-9} and 3.7×10^{-8}, respectively, at 25 °C.

    a. Write the solubility product equations for the precipitates that are expected to form.

    $K_{sp} = [Pb^{2+}][F^{1-}]^2$

    $K_{sp} = [Pb^{2+}][I^{1-}]^2$

    b. State the initial concentrations of I^{1-} and F^{1-} in the solution.

    Initial $[I^{1-}] = 0.0025\ M$

    Initial $[F^{1-}] = 0.0025\ M$

    c. Which precipitate will form first as lead(II) nitrate is added?

    Lead(II) iodide will form first because it has a smaller K_{sp} *(it is less soluble) than lead(II) fluoride.*

    d. What volume of lead(II) nitrate will be required for the first precipitate to form? (Assume the total change in solution volume is negligible.)

    $K_{sp} = [Pb^{2+}][I^{1-}]^2$

    $8.7 \times 10^{-9} = [Pb^{2+}](0.0025)^2$

    $[Pb^{2+}] = 0.0014\ M$

    $(0.0014\ M)(1000\ mL) = (x)(1.00\ M)$

    $x = 1.4\ mL$

    e. What volume of lead(II) nitrate will be required for the second precipitate to form?

    $K_{sp} = [Pb^{2+}][F^{1-}]^2$

    $3.7 \times 10^{-8} = [Pb^{2+}](0.0025)^2$

    $[Pb^{2+}] = 0.0059\ M$

    $(0.0059\ M)(1000\ mL) = (x)(1.00\ M)$

    $x = 5.9\ mL$

    f. When the second precipitate begins to form, what is the concentration of halide ion that remains unprecipitated from the first precipitate?

    $K_{sp} = [Pb^{2+}][I^{1-}]^2$

    $8.7 \times 10^{-9} = (0.0059\ M)[I^{1-}]^2$

    $[I^{1-}] = 0.0012\ M$

25. A 0.85 M solution of silver nitrate is slowly added to a solution containing 0.018 M chloride ions and 0.018 M chromate ions. What is the concentration of chloride ions just as silver chromate begins to precipitate? The K_{sp} values for silver chloride and silver chromate are 1.77×10^{-10} and 1.12×10^{-12}, respectively, at 25 °C.

    $K_{sp} = 1.12 \times 10^{-12} = [Ag^{1+}]^2[CrO_4^{2-}]$

    $1.12 \times 10^{-12} = [Ag^{1+}]^2(0.018\ M)$

    $[Ag^{1+}] = 7.89 \times 10^{-6}\ M$

    $K_{sp} = 1.77 \times 10^{-10} = [Ag^{1+}][Cl^{1-}]$

    $1.77 \times 10^{-10} = (7.89 \times 10^{-6}\ M)[Cl^{1-}]$

    $[Cl^{1-}] = 2.24 \times 10^{-5}\ M$

Teacher Resources – Fractional Precipitation

Learning Objectives

1. Predict which precipitate will form first when a solution is added to a mixture of ions.
2. Calculate the concentration of added solution needed to form a precipitate.
3. Calculate the concentration of ions remaining in solution when a second precipitate starts to form.

Prerequisites

1. Students should be comfortable with using K_{sp} to calculate the concentration of an ion needed to form a precipitate.
2. Students should be able to compare Q_{sp} and K_{sp} to determine if a precipitate will form.
3. Students should be able to calculate the concentration of a solution after being diluted.

Assessment Questions

1. A solution of sodium sulfate is added dropwise to a solution containing calcium ions and strontium ions. What information is needed to predict which precipitate will form first?
   a. Volumes of the two solutions.
   b. Concentrations of all the salts in the two solutions.
   c. K_{sp} values for possible precipitate combinations.
   d. Balanced chemical reactions for the precipitate formation.
2. A 1.00 M solution of lead(II) nitrate is added dropwise to a solution containing 0.0030 M sodium carbonate and 0.0030 M sodium chromate. The K_{sp} values of lead(II) carbonate and lead(II) chromate are 7.4×10^{-14} and 2.8×10^{-13}, respectively, at 25 °C. Which precipitate will form first when lead(II) nitrate is added?
3. A 1.00 M solution of lead(II) nitrate is added dropwise to a solution containing 0.0030 M sodium carbonate and 0.0030 M sodium chromate. The K_{sp} values of lead(II) carbonate and lead(II) chromate are 7.4×10^{-14} and 2.8×10^{-13}, respectively, at 25 °C. Calculate the concentration of carbonate ions remaining in solution when lead(II) chromate begins to precipitate.

Assessment Target Responses

1. *c*
2. *Lead(II) carbonate*
3. $[CO_3^{2-}] = 7.9 \times 10^{-4}\ M$

Teacher Tips

- Note that in all of the examples in this activity, the concentration of the added ion that forms the precipitate is significantly larger than the concentrations of the ions in solution being precipitated. This is strategic. If the concentrations were of the same order, we could not assume that a negligible amount of added ion was used in the precipitation, thus keeping the concentration of that ion in solution "constant" throughout the addition. This becomes a much more complicated problem that is more suited to a junior college level course.
- One interesting application of this technique is Marie Curie and her discovery of radium. Starting with one ton of a special uranium-depleted ore, Marie Curie carried out a series of exhausting large-scale precipitation reactions. She obtained 100 milligrams of a new, radioactive element—radium, the heaviest member of the alkaline earth metals. The separation worked because the solubility of alkaline earth metals decreases as you go down the column in the Periodic Table. Radium chloride is ever-so-slightly less soluble than barium chloride. Working with concentrated hydrochloric acid, Marie Curie carried out many, many repeat fractional crystallization reactions with a mixture of barium and radium chlorides from the ore. With each successive crystallization, the precipitate gradually became enriched in the amount of the less soluble radium fraction, until finally almost pure radium chloride was obtained.

Alignment with AP Chemistry Frameworks

- **Essential Knowledge 6.C.3:** The solubility of a substance can be understood in terms of chemical equilibrium.

  Learning Objective 6.21 The student can predict the solubility of a salt, or rank solubility of salts, given the relevant K_{sp} values.

  Learning Objective 6.22 The student can interpret data regarding solubility of salts to determine, or rank, the relevant K_{sp} values.

  Learning Objective 6.23 The student can interpret data regarding the relative solubility of salts in terms of factors (common ions, pH) that influence the solubility.

Common Ion Effect on Acid Ionization

How is the ionization of a weak acid affected by other ion species in solution?

Why?

The ionization constant (K_a) for a weak acid allows chemists to predict the concentration of ions in solution at equilibrium. At this point you have learned to solve these types of problems if the weak acid is ionized in water. But what if the beaker contains a solution that already has some ions dissolved in it? Can the weak acid still ionize to the same extent? Does the percent ionization change?

Model 1 – Weak Acid Equilibrium

Note: Proceed to Question 1 on the next page. Do not fill in these tables until instructed to do so.

$$HCH_3COO\,(aq) + H_2O \rightarrow H_3O^{1+}(aq) + CH_3COO^{1-}(aq) \quad K_a = 1.76 \times 10^{-5}$$

Beaker 1

	HCH_3COO	H_3O^{1+}	CH_3COO^{1-}
Initial	1.00 M	0 M	0 M
Change	$-x$	$+x$	$+x$
Equilibrium	$1.00 - x$	x	x

Percent Acid Ionization = *0.420%*

$$1.76 \times 10^{-5} = \frac{(x)(x)}{1.00 - x} \approx x^2$$

$x \approx 0.00420\ M$

Beaker 2

	HCH_3COO	H_3O^{1+}	CH_3COO^{1-}
Initial	1.00 M	0 M	0.200 M
Change	$-x$	$+x$	$+x$
Equilibrium	$1.00 - x$	x	$0.200 + x$

Percent Acid Ionization = *0.00880%*

$$1.76 \times 10^{-5} = \frac{(x)(0.200 + x)}{1.00 - x} \approx 0.200x$$

$x \approx 8.80 \times 10^{-5}\ M$

Beaker 3

	HCH_3COO	H_3O^{1+}	CH_3COO^{1-}
Initial	1.00 M	0 M	0.500 M
Change	$-x$	$+x$	$+x$
Equilibrium	$1.00 - x$	x	$0.500 + x$

Percent Acid Ionization = *0.00352%*

$$1.76 \times 10^{-5} = \frac{(x)(0.500 + x)}{1.00 - x} \approx 0.500x$$

$x \approx 3.52 \times 10^{-5}\ M$

Beaker 4

	HCH_3COO	H_3O^{1+}	CH_3COO^{1-}
Initial	1.00 M	0.200 M	0 M
Change	$-x$	$+x$	$+x$
Equilibrium	$1.00 - x$	$0.200 + x$	x

Percent Acid Ionization = *0.00880%*

$$1.76 \times 10^{-5} = \frac{(x)(0.200 + x)}{1.00 - x} \approx 0.200x$$

$x \approx 8.80 \times 10^{-5}\ M$

1. Match each of the following descriptions with one of the beakers in Model 1. In each case assume that the change in volume as the solid(s) are added is minimal. *Hint:* Calculate the molarity of any soluble ions after the solids have dissolved or solutions have been mixed.

   a. Beaker *1* contains 500.0 mL of 1.00 M acetic acid.

   b. Beaker *3* contains 0.250 mole of solid sodium acetate, $NaCH_3COO$, dissolved into 500.0 mL of 1.00 M acetic acid.

   c. Beaker *2* contains 0.0500 mole of solid zinc acetate, $Zn(CH_3COO)_2$, dissolved into 500.0 mL of 1.00 M acetic acid.

   d. Beaker *4* contains 250.0 mL of 0.40 M hydrochloric acid mixed with 250.0 mL of 2.00 M acetic acid.

2. Based on the acid ionization constant, K_a, for acetic acid provided in Model, 1 do you expect most of the acid molecules to ionize in any of the four beakers?

   No, the acid ionization constant, K_a, *for acetic acid is very small, so only a small amount will ionize in any of the beakers.*

3. Three of the beakers in Model 1 contain a **common ion** in solution.

   a. Which beakers in Model 1 contain a common ion?

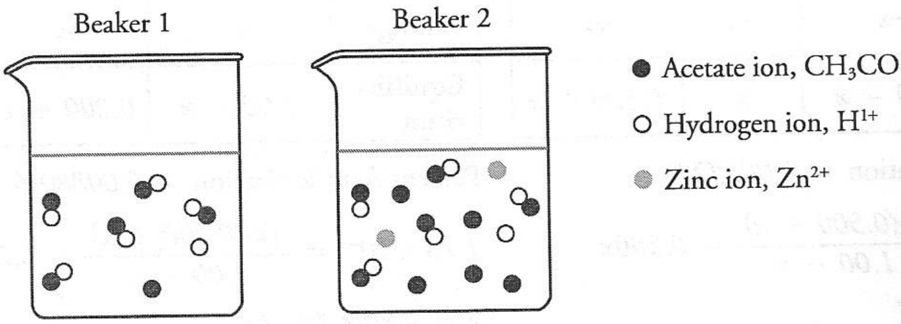
   Beakers 2, 3 and 4 contain a common ion.

   b. Consider the source of the common ion in each beaker. Does the common ion come from the weak acid molecules? If no, explain the source of the common ion.

   The common ion does not come from the weak acid. It is from a salt of the conjugate base or from another acid.

4. Predict what will be in Beakers 1 and 2 when the systems in those beakers reach equilibrium. Use particulate drawings below to communicate your predictions. You may omit water molecules for clarity.

   Note: *The exact ratio of ionized to molecular acetic acid units is not critical since the students have not done any calculations at this point. What is important is that they show the majority of acetic acid in the molecular state, the ratio of acetate ions to hydrogen ions is correct, and they show an increased number of acetate ions in Beaker 2 compared to Beaker 1.*



5. Write the equation for the acid ionization constant, K_a, for this acid.

$$K_a = \frac{[H_3O^+][CH_3COO^{1-}]}{[CH_3COOH]}$$

6. Divide the work among group members to fill in each of the tables in Model 1. Use the acid ionization constant to find the final concentrations of the molecular and ionic species in each beaker (excluding water). Add this to Model 1. (Work space for these calculations has been provided in Model 1.)

See Model 1.

7. Calculate the percent ionization of the weak acid in each beaker in Model 1 using the information from the tables. Add this information to Model 1.

See Model 1.

8. Does the presence of a common ion with a weak acid increase or decrease the percent ionization of the weak acid? Support your answer with evidence from Model 1.

The presence of a common ion in solution with a weak acid decreases the percent ionization. The weak acid in water had 0.420% ionization, but when a common ion was present, the percent ionization was 0.00880% or 0.00352%.

9. According to Model 1, as the concentration of the common ion is increased, how does the percent ionization of the weak acid change? Support your answer with evidence from Model 1.

As the concentration of the common ion increased, the percent ionization of the weak acid decreased. When the common acetate ion had a concentration of 0.200 M, the percent ionization of the weak acid was 0.00880%. When the acetate ion increased to 0.500 M, the percent ionization of the weak acid decreased to 0.00352%.

10. Are the data in Model 1 consistent with LeChâtelier's Principle? Support your answer with specific examples from Model 1.

According to LeChâtelier's Principle, as the concentration of an equilibrium species increases, the reaction should shift in a direction that uses up that species. In Model 1, as the concentration of the common ion increases, the weak acid percent ionization is lower (the reaction shifts left). This is consistent with LeChâtelier's Principle.

11. Consider the four beakers below. Rank the beakers in terms of percent ionization of the weak acid from lowest to highest percent. The weak acid ionization constant for hydrofluoric acid is 6.31×10^{-4}.

Beaker 1	**Beaker 2**	**Beaker 3**	**Beaker 4**
0.025 M HF	0.025 M HF	0.025 M HF	0.025 M HF
	0.010 M NaF	0.010 M BaF_2	0.010 M HCl

The weak acid would have the lowest percent ionization in Beaker 3 as this beaker has the highest common ion concentration assuming NaF, BaF_2, and HCl are strong electrolytes. Beakers 2 and 4 would have the next lowest percent ionization as they also contain a common ion. Beaker 1 would have the highest percent ionization.

12. The acid ionization constant for benzoic acid (C_6H_5COOH) is 6.46×10^{-5}. Compare the percent ionization of 1.00 M benzoic acid in water with its percent ionization in 0.500 M sodium benzoate solution. Support your comparison with calculations similar to those in Model 1.

$$C_6H_5COOH\,(aq) + H_2O\,(l) \leftrightarrow H_3O^{1+}\,(aq) + C_6H_5COO^{1-}\,(aq)$$

Ionization of C_6H_5COOH in water

	C_6H_5COOH	H_3O^{1+}	$C_6H_5COO^{1-}$
Initial	*1.00 M*	*0 M*	*0 M*
Change	$-x$	$+x$	$+x$
Equilibrium	*1.00 M*	x	x

$$K_a = \frac{[H_3O^{1+}][C_6H_5COO^{1-}]}{[C_6H_5COOH]} = \frac{(x)(x)}{(1.00 - x)}$$

$$6.46 \times 10^{-5} \approx \frac{x^2}{1.00}$$

$$x \approx 0.00804\ M$$

Percent ionization = 0.804%

Ionization of C_6H_5COOH in 0.500 M sodium benzoate solution

	C_6H_5COOH	H_3O^{1+}	$C_6H_5COO^{1-}$
Initial	*1.00 M*	*0 M*	*0.500 M*
Change	$-x$	$+x$	x
Equilibrium	*1.00 M*	x	$0.500 + x$

$$K_a = \frac{[H_3O^{1+}][C_6H_5COO^{1-}]}{[C_6H_5COOH]} = \frac{(x)(0.500 + x)}{(1.00 - x)}$$

$$6.46 \times 10^{-5} \approx \frac{0.500x}{1.00}$$

$$x \approx 0.00804\ M$$

Percent ionization = 0.0129%

Extension Questions

13. The pH of the solutions in the four beakers in Model 1 was measured. Match each pH with the correct beaker.

pH = 0.7 Beaker *4*

pH = 4.0 Beaker *2*

pH = 2.4 Beaker *1*

pH = 4.5 Beaker *3*

14. You have seen that the presence of a common ion in solution will decrease the percent ionization of a weak acid in solution. Provide two things that could be done to a solution to increase the percent ionization of a weak acid.

A base could be added that would react with the H_3O^{1+} *in the weak acid solution. The removal of this species would shift the reaction right and cause more ionization of the weak acid.*

A salt could be added that would precipitate with the conjugate base. This would decrease the concentration of the conjugate base, shifting the reaction to the right and causing more ionization of the weak acid.

Teacher Resources – Common Ion Effect on Acid Ionization

Learning Objectives

1. Describe the effect on the percent ionization of a weak acid when a common ion is present in solution.
2. Calculate the percent ionization of a weak acid when a common ion is present in solution.

Prerequisites

1. Students should be comfortable solving equilibrium problems with weak acids.
2. Students should be able to calculate percent ionization of a weak acid.
3. Students should be comfortable with LeChâtelier's Principle for predicting the direction of shift in a chemical equilibrium.

Assessment Questions

1. When a common ion is present in solution with a weak acid, the percent ionization of the weak acid is
   a. increased.

   b. decreased.

   c. unchanged.

   d. difficult to predict.
2. Benzoic acid is a weak acid. Which of the following solutions will have the highest pH?
   a. 0.0010 M benzoic acid in water.

   b. 0.0010 M benzoic acid in 0.0025 M sodium benzoate.

   c. 0.0010 M benzoic acid in 0.0025 M calcium benzoate.

   d. 0.0010 M benzoic acid in 0.0025 M hydrochloric acid.
3. The acid ionization constant, K_a, for propionic acid, $HC_3H_5O_2$, is 1.34×10^{-5}. Calculate the percent ionization of a 0.100 M propionic acid solution in water and the percent ionization of 0.100 M propionic acid in the presence of 0.100 M sodium propionate.

Assessment Target Responses

1. *b*
2. *c*

3. *In water:*

$$K_a = \frac{[H_3O^{1+}][CH_3CH_2COO^{1-}]}{[CH_3CH_2COOH]}$$

$$1.34 \times 10^{-5} = \frac{(x)(x)}{0.100 - x}$$

$$x = 0.00116\ M$$

$$\text{Percent ionization} = 1.16\%$$

In sodium propionate:

$$K_a = \frac{[H_3O^{1+}][CH_3CH_2COO^{1-}]}{[CH_3CH_2COOH]}$$

$$1.34 \times 10^{-5} = \frac{(0.100 - x)(x)}{0.100 - x}$$

$$x = 1.34 \times 10^{-5}\ M$$

$$\text{Percent ionization} = 0.0134\%$$

Teacher Tips

- Before doing this activity, it may be helpful to demonstrate the properties of a buffer. Prepare four large test tubes. Fill two with water and two with buffer solution. Add a few drops of universal indicator to each of the test tubes. Show students the change in pH (indicator color) when 10 drops of 0.100 M hydrochloric acid is added to water. Compare that to what happens when the hydrochloric acid is added to the buffer. Repeat with 0.100 M sodium hydroxide. Follow all laboratory safety and disposal guidelines.
- A very common mistake for students when given a weak acid and conjugate salt is to write a chemical reaction between the two species.

  $CH_3COOH + NaCH_3COO \leftrightarrow ?$

  This does not work.

  Stress to students that the weak acid and the common ion (from the dissociated salt) are on **opposite** sides of the chemical reaction. They are two species in the same equilibrium system.

Alignment with AP Chemistry Framework

- **Essential Knowledge 6.C.1:** Chemical equilibrium reasoning can be used to describe the proton-transfer reactions of acid–base chemistry.

  Learning Objective 6.12 The student can reason about the distinction between strong and weak acid solutions with similar values of pH, including the percent ionization of the acids, the concentrations needed to achieve the same pH, and the amount of base needed to reach the equivalence point in a titration.

Buffers

How can a solution neutralize both acids and bases?

Why?

Buffer solutions are a mixture of substances that have a fairly constant pH regardless of addition of acid or base. They are used in medicine, industry and manufacturing to keep the pH of a solution stable regardless of other reactions that might be occurring. You have buffers in your blood, for example, because the proper function of enzymes is dependent on the pH of your blood staying in a narrow range. Eating, breathing and exercising can all alter the acidity or basicity of your blood, but the buffers in your blood help control the pH and keep all of your enzymes working properly.

Model 1 – Comparing Solutions

Beaker A: 100 mL Pure Water

$$H_2O + H_2O \leftrightarrow H_3O^{1+}(aq) + OH^{1-}(aq)$$

WA	*WB*	*CA*	*CB*
		$1.00 \times 10^{-7} M$	*$1.00 \times 10^{-7} M$*

Beaker B: 100 mL of 1.00 M HCl

$$HCl(aq) + H_2O \rightarrow H_3O^{1+}(aq) + Cl^{1-}(aq)$$

SA	*WB*	*CA*	*CB*
~0 M		*1.00 M*	*1.00 M*

Beaker C: 100 mL of 1.00 M HNO_2
$K_a = 4.6 \times 10^{-4}$

$$HNO_2(aq) + H_2O \leftrightarrow H_3O^{1+}(aq) + NO_2^{1-}(aq)$$

WA	*WB*	*CA*	*CB*
0.98 M		*0.021 M*	*0.021 M*

Beaker D: 100 mL of 1.00 M HNO_2
with 100 mL of 1.00 M $NaNO_2$

$$HNO_2(aq) + H_2O \leftrightarrow H_3O^{1+}(aq) + NO_2^{1-}(aq)$$

WA	*WB*	*CA*	*CB*
0.50 M		*$4.6 \times 10^{-4} M$*	*0.50 M*

1. For each beaker in Model 1 write SA (strong acid), SB (strong base), WA (weak acid), WB (weak base), CA (conjugate acid) or CB (conjugate base) under each molecule or ion in the reaction.

   See Model 1.

2. For each beaker in Model 1 write the final or equilibrium concentrations of the molecules or ions under each species in the reaction. Divide the work among group members. If calculations are required, show your work below.

   See Model 1.

3. Imagine that 1.00 M sodium hydroxide was added dropwise to each of the beakers in Model 1. List the species in each beaker that would react with this base and neutralize significant quantities (at least 0.05 mole) of it. If neutralization is not likely to occur, write "none."

Beaker A	Beaker B	Beaker C	Beaker D
None	*H_3O^{1+}*	*HNO_2*	*HNO_2*

4. Imagine that 1.00 M hydrochloric acid was added dropwise to each of the beakers in Model 1. List the species in each beaker that could react with this acid and neutralize significant quantities (at least 0.05 mole) of it. If neutralization is not likely to occur, write "none."

Beaker A	Beaker B	Beaker C	Beaker D
None	*None*	*None*	NO_2^{1-}

5. Which beaker in Model 1 was able to neutralize significant quantities of both acid and base?

   Beaker D can neutralize both acid and base.

Read This!

A buffer solution is one that can neutralize both small quantities of acid and small quantities of base. This is possible because the solution contains both a weak acid and its conjugate base species in equilibrium. By neutralizing any acid or base that is added, the solution can keep a fairly constant pH.

6. Which beaker in Model 1 contains a buffer?

   Beaker D contains a buffer.

7. One way to make a buffer solution is to mix a weak acid solution with a solution of a salt of its conjugate base. Explain why both the weak acid and the salt of its conjugate (common ion) are required to make a buffer.

   For a buffer to be able to neutralize both acid and base and keep the pH of the solution constant, both an acid and a base must be present. In a buffer, the weak acid can neutralize bases and the conjugate base (from the salt) can neutralize acids. Direct addition of a salt solution of the conjugate base is necessary to ensure there is enough of the conjugate base in solution. Weak acids do not dissociate enough to give sufficient conjugate base to the solution.

8. Circle all the combinations below that would make a buffer solution when mixed in equal volumes.

   1.0 M HCl and 1.0 M NaCl

   1.0 M HNO_2 and 1.0 M HNO_3

   [✓ 1.0 M NH_4Cl and 1.0 M NH_3]

   1.0 M CH_3COOH and 1.0 M NaCl

   [✓ 1.0 M HF and 1.0 M NaF]

   1.0 M H_2SO_4 and 1.0 M Na_2SO_4

9. Choose one of the buffers you circled in Question 8 and describe how it would neutralize both acids and bases to keep the pH fairly constant.

   Answers will vary. The buffer made with ammonia and ammonium will neutralize additional acids with the NH_3 and neutralize additional bases with the NH_4^{1+} ion.

STOP

Model 2 – pH of Buffer Solutions

Beaker 1

100 mL 1.0 M NH_4Cl and 100 mL 1.0 M NH_3

K_a for $NH_4^{1+} = 5.6 \times 10^{-10}$ pK$_a$ = *9.25*

$NH_4^{1+} + H_2O \leftrightarrow H_3O^{1+} + NH_3$

	NH_4^{1+}	H_3O^{1+}	NH_3
Initial	*0.50 M*	*0 M*	*0.50 M*
Change	$-x$	$+x$	$+x$
Equilibrium	$0.50 - x$	x	$0.50 + x$

$$5.6\times 10^{-10} = \frac{(x)(0.50 + x)}{0.50 - x} \approx x$$

$x \approx 5.6\times 10^{-10}$ M

pH = *9.25*

Beaker 2

100 mL 1.0 M HF and 100 mL 1.0 M NaF

K_a for HF = 3.5×10^{-4} pK$_a$ = *3.46*

$HF + H_2O \leftrightarrow H_3O^{1+} + F^{1-}$

	HF	H_3O^{1+}	F^{1-}
Initial	*0.50 M*	*0 M*	*0.50 M*
Change	$-x$	$+x$	$+x$
Equilibrium	$0.50 - x$	x	$0.50 + x$

$$3.5\times 10^{-4} = \frac{(x)(0.50 + x)}{0.50 - x} \approx x$$

$x \approx 3.5\times 10^{-4}$ M

pH = *3.46*

Beaker 3

100 mL 1.0 M H_2CO_3 and 100 mL 1.0 M $NaHCO_3$

K_a for $H_2CO_3 = 4.4 \times 10^{-7}$ pK$_a$ = *6.36*

$H_2CO_3 + H_2O \leftrightarrow H_3O^{1+} + HCO_3^{1-}$

	H_2CO_3	H_3O^{1+}	HCO_3^{1-}
Initial	*0.50 M*	*0 M*	*0.50 M*
Change	$-x$	$+x$	$+x$
Equilibrium	$0.50 - x$	x	$0.50 + x$

$$4.4\times 10^{-7} = \frac{(x)(0.50 + x)}{0.50 - x} \approx x$$

$x \approx 4.4\times 10^{-7}$ M

pH = *6.36*

Beaker 4

100 mL 1.0 M HF and 300 mL 1.0 M NaF

K_a for HF = 3.5×10^{-4} pK$_a$ = *3.46*

$HF + H_2O \leftrightarrow H_3O^{1+} + F^{1-}$

	HF	H_3O^{1+}	F^{1-}
Initial	*0.25 M*	*0 M*	*0.75 M*
Change	$-x$	$+x$	$+x$
Equilibrium	$0.25 - x$	x	$0.75 + x$

$$3.5\times 10^{-4} = \frac{(x)(0.75 + x)}{0.25 - x} \approx x$$

$x \approx 1.17\times 10^{-4}$ M

pH = *3.93*

10. Model 2 describes four buffer solutions made by mixing two solutions together—a weak acid and the salt of its conjugate base. Write a net ionic equation for the chemical equilibrium working in each buffer in the space above each table in Model 2.

    See Model 2.

11. Use the tables to find the pH of each buffer solution in Model 2. Divide the work evenly among group members. Be sure to consider how the molarities of the solutions will change when the two parts of the buffer are mixed.

    See Model 2.

12. Do all buffers keep solutions at a neutral pH? Justify your answer with data from Model 2.

    No, none of the buffers in Model 2 have a pH of 7. The closest is the carbonic acid/sodium bicarbonate buffer with a pH of 6.36.

13. Calculate the pK_a's for the weak acids in each of the buffer solutions described in Model 2 and list them in the model.

    See Model 2. $pK_a = -\log(K_a)$

14. How are the pK_a values of the weak acids related to the pH of the buffer system that is made when equal molarities of acid and conjugate base are combined?

    The pH of the resulting buffer solution is equal to the pK_a *of the weak acid used to make the buffer. The pH of an ideal buffer should be within ±1 of the weak acid's* pK_a*.*

15. When unequal molarities of acid and conjugate base are combined to make a buffer (as in beaker 4 of Model 2), does the pH change significantly from the pK_a of the weak acid? Support your answer with data from Model 2.

    No, the pH of the buffer solution is not changed significantly. Beaker 2 in Model 2 has a pH of 3.46, while beaker 4 has a pH of 3.77.

16. An industrial process requires a constant pH of 3.00. The weak acids available in the warehouse are benzoic acid ($HC_7H_3O_2$), $K_a = 6.3 \times 10^{-5}$, nitrous acid (HNO_2), $K_a = 7.2 \times 10^{-4}$, phosphorous acid (H_3PO_3), $K_a = 3.7 \times 10^{-2}$, and hydrocyanic acid (HCN), $K_a = 6.2 \times 10^{-10}$.

    a. Which of the four acids would be best to make a buffer for the industrial process?

    The pK_a *for nitrous acid is 3.14 so that would be the best weak acid to use for a buffer at* $pH = 3.00$*.*

    b. What other chemical(s) are needed to prepare the buffer?

    To make the buffer you would also need a salt of the conjugate base, such as $NaNO_2$*.*

Extension Questions

17. Would either of the beakers you circled in Question 8 be able to neutralize unlimited quantities of acid or base? If no, explain what the limiting factor would be.

No, eventually either the weak acid or the conjugate base would become the limiting reactant and could no longer neutralize added acid or base. The molarity of those components in the buffer would be the limiting factor. Higher molarity solutions could neutralize more.

18. Circle all the combinations below that would make a buffer solution when mixed. *Note:* In all cases a neutralization reaction will occur. Consider what the products of the neutralization will be and how much of each species will be present when the reaction is completed.

a. 100 mL of 1.0 M HCl with 100 mL of 1.0 M NaOH

b. 100 mL of 1.0 M HNO_2 with 100 mL of 1.0 M NaOH

[✓ *c.* 100 mL of 1.0 M sodium acetate with 100 mL of 0.50 M HCl]

d. 100 mL of 1.0 M HCl with 50 mL of 1.0 M NaOH

[✓ *e.* 100 mL of 1.0 M HNO_2 with 50 mL of 1.0 M NaOH]

[✓ *f.* 100 mL of 1.0 M acetic acid with 100 mL of 0.50 M NaOH]

19. A buffer solution is made by mixing equal moles of a weak acid and the salt of its conjugate ion. Would the resulting solution have a pH equal to, greater than, or less than the pH of the weak acid solution in water alone? Justify your reasoning.

The buffer solution would have a higher pH than the weak acid in water. The presence of a common ion shifts the acid ionization reaction to the left, decreasing the percent ionization and lowering the concentration of hydronium ion in the solution.

20. One buffer system in the bloodstream of animals is the carbonic acid/bicarbonate buffer.

$$H_2CO_3 + H_2O \leftrightarrow HCO_3^{1-} + H_3O^+$$

The carbonic acid in the bloodstream is formed by the combination of carbon dioxide gas and water. This is a reversible process.

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

Therefore, the whole buffer system is linked to the respiratory system of the animal and the concentration of dissolved CO_2 gas in the animal's bloodstream.

a. What species in the blood buffer system neutralizes excess acid in the body?

The bicarbonate ion neutralizes excess acid.

b. What species in the blood buffer system neutralizes excess base in the body?

The carbonic acid neutralizes excess base.

Teacher Resources – Buffers

Learning Objectives

1. Identify a buffer solution as a mixture of a weak acid and a salt of a conjugate base in solution.
2. Explain why a buffer must contain both a weak acid and a conjugate base salt in order to neutralize both acids and bases.

Prerequisites

1. Students should be able to identify strong and weak acids and bases in a chemical reaction.
2. Students should understand neutralization reactions between acids and bases.
3. Students should be comfortable solving equilibrium problems with weak acids including those with common ions present.
4. Students should be able to calculate the pK_a of a weak acid when given the K_a.

Assessment Questions

1. Which of the scenarios below describes a buffer solution?
   - *a.* Solid sodium fluoride is added to 100 mL of 0.100 M hydrofluoric acid.
   - *b.* Solid sodium nitrate is added to 100 mL of 0.100 M nitric acid.
   - *c.* 50 mL of 0.100 M hydrochloric acid and 50 mL of 0.100 M sodium chloride solution are mixed in a beaker.
   - *d.* 50 mL of 0.200 sulfuric acid and 50 mL of 0.200 M sodium bisulfate solution are mixed in a beaker.
2. Which of the following solutions would result in a buffer with a pH of approximately 4.0?
   - *a.* 100 mL of 1.0 M H_2CO_3 ($K_a = 4.4 \times 10^{-7}$) and 100 mL of 1.0 M $NaHCO_3$
   - *b.* 100 mL of 1.0 M HF ($K_a = 3.47 \times 10^{-4}$) and 100 mL of 1.0 M NaF
   - *c.* 100 mL of 1.0 M HCN ($K_a = 6.2 \times 10^{-10}$) and 100 mL of 1.0 M NaCN
   - *d.* 100 mL of 1.0 M $HC_7H_3O_2$ ($K_a = 6.3 \times 10^{-5}$) and 100 mL of 1.0 M $NaC_7H_3O_2$
3. Explain why a buffer solution cannot be made with a strong acid.

Assessment Target Responses

1. *a*
2. *d*
3. *A strong acid will not result in a buffer because the conjugate base of a strong acid is not a strong enough base to neutralize other acids. If another weak base was added to the strong acid solution, the strong acid would simply neutralize the weak base and no buffer solution would result.*

Teacher Tips

- Before doing this activity, it may be helpful to demonstrate the properties of a buffer. Prepare four large test tubes. Fill two with water and two with a buffer solution. Add a few drops of universal indicator to each of the test tubes. Show students the change in pH (indicator color) when 10 drops of 0.100 M hydrochloric acid is added to water. Compare that to what happens when the hydrochloric acid is added to the buffer. Repeat with 0.100 M sodium hydroxide. Follow all laboratory safety and disposal guidelines.
- A major student misconception about buffers is that they will hold a solution pH at 7 making all buffers neutral. The questions following Model 2 should help to repair that misconception.

Alignment with AP Chemistry Framework

- **Essential Knowledge 6.C.2:** The pH is an important characteristic of aqueous solutions that can be controlled with buffers. Comparing pH to pK_a allows one to determine the protonation state of a molecule with a labile proton.

  Learning Objective 6.18 The student can design a buffer solution with a target pH and buffer capacity by selecting an appropriate conjugate acid–base pair and estimating the concentrations needed to achieve the desired capacity.

  Learning Objective 6.19 The student can relate the predominant form of a chemical species involving a labile protone (i.e., protonated/deprotonated form of a weak acid) to the pH of a solution and the pK_a associated with the labile proton.

  Learning Objective 6.20 The student can identify a solution as being a buffer solution and explain the buffer mechanism in terms of the reactions that would occur on addition of acid or base.

Strength of Acids

How does the molecular structure of an acid influence its strength?

Why?

Bronsted-Lowry acids (H^{1+} ion) are proton donors. A stronger acid is more likely to give up a proton. The structure of an acid molecule, and the atoms remaining behind have a lot to do with the ease of donating the proton.

Model 1 – Donating a Hydrogen Ion

$$HCl + H_2O \rightarrow H_3O^{1+} + Cl^{1-}$$

1. Refer to Model 1.

   a. Which reactant acts as the acid?

   The HCl is the acid.

   b. Which reactant acts as the base?

   Water is acting as the base.

   c. What is the conjugate base to the reactant acid?

   The conjugate base is a chloride ion (Cl^{1-}).

2. Add a curved arrow in Model 1 to show the transfer of the proton (H^{1+} ion) from the acid to the base in the reaction.

   See Model 1.

3. Describe the bonds that are broken and formed during the reaction in Model 1.

   The bond between the hydrogen and chlorine atoms must break. The bond between the acidic hydrogen ion and the oxygen of the water molecule must form.

4. If the bond that was broken was a relatively strong bond, would you expect the acid to be a stronger or weaker acid? Justify your reasoning.

   If the bond was relatively strong, the acid would be weaker because it would be less likely that the hydrogen ion would get donated. Too much energy would be needed to break the bond.

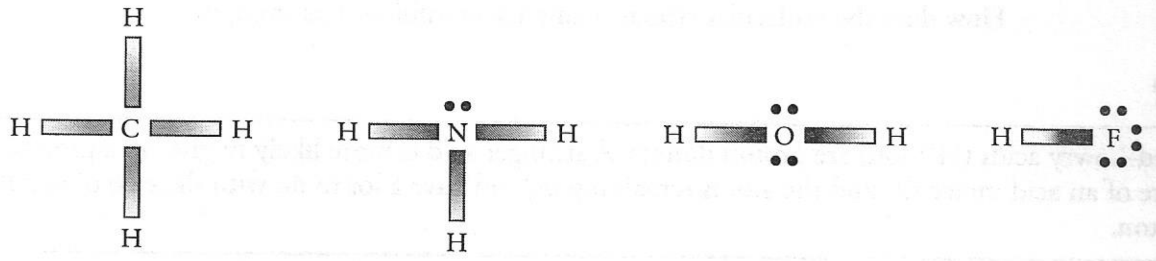
5. During the reaction in Model 1, one atom loses an electron and another gains an electron. Which atom lost the electron, and which atom gained the electron?

   The hydrogen atom lost its electron. The chlorine atom gained the electron, becoming a chloride ion.

6. If the atom receiving the electron (the conjugate base) was more electronegative (and thus could hold the extra electron more tightly) would you expect the acid to be a stronger or weaker acid? Justify your reasoning.

   If the conjugate base was more electronegative, it would be more stable with an additional electron and thus promote proton donation, making the acid stronger.

Model 2 – Comparing Binary Acid Strength



$K_a = 1.0 \times 10^{-48}$ $K_a = 1.0 \times 10^{-38}$ $K_w = 1.0 \times 10^{-14}$ $K_a = 6.3 \times 10^{-4}$

7. Which acid in Model 2 is most likely to donate a proton (H^{1+} ion)? Justify your reasoning.

   Hydrofluoric acid is most likely to donate a proton because it has the largest K_a *value. Larger* K_a *values correspond to stronger acids.*

8. Consider the center atoms in the molecules in Model 2. Locate those atoms on the periodic table. Based on their location on the periodic table, which center atom is the most electronegative?

   Fluorine is the most electronegative because it is farthest to the right on the periodic table.

9. Consider Model 2.

   a. Which molecule contains bonds that are the most polar?

   Hydrofluoric acid has the most polar bonds. That is, the electronegativity difference between H and F is largest.

   b. How is the extent of bond polarity illustrated in Model 2?

   The negative end of a polar bond is black while the positive end is white.

10. According to the data in Model 2, how does the polarity of the bond between the hydrogen atom and the center atom of a binary acid affect the strength of the acid?

    When the bond between the hydrogen atom and the center atom is more polar, the acid is stronger.

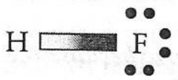
11. How might the polarity of the bond and the electronegativity of the center atom make it more likely for the hydrogen ion to leave the molecule? *Hint:* Consider what is left behind when the hydrogen ion leaves.

    If the center atom is more electronegative, it can hold more tightly to the electron that the hydrogen ion leaves behind. The electronegative atom pulls electron density towards itself to such a degree that it becomes easy for the hydrogen ion to break away. This makes it easier for the hydrogen to leave and makes the acid stronger.

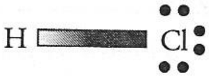
12. Predict which substance would be the stronger acid: hydrosulfuric acid (H_2S) or hydrochloric acid (HCl). Explain your reasoning.

    Chlorine is more electronegative than sulfur, so hydrochloric acid would be the stronger acid.

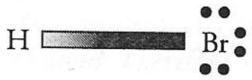
Model 3 – More Binary Acids



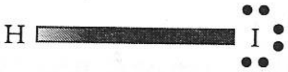
$K_a = 6.3 \times 10^{-4}$



$K_a = 1.0 \times 10^{7}$



$K_a = 1.0 \times 10^{9}$



$K_a = 1.0 \times 10^{10}$

13. Which acid in Model 3 is least likely to donate a proton (H^{1+} ion)? Justify your reasoning.

    Hydrofluoric acid has the smallest acid dissociation constant (K_a), so it would be least likely to donate a proton.

14. Consider the atoms in the molecules in Model 3 that are bonded to hydrogen. Locate those atoms on the periodic table. Based on their location on the periodic table, which atom is the most electronegative?

    The most electronegative center atom is fluorine.

15. Can bond polarity and electronegativity of the nonhydrogen atom explain the trend in acid strength shown in Model 3? Use complete sentences to explain why or why not.

    No, in this case the most polar bond is in hydrofluoric acid—the weakest acid. This is not consistent with what was discovered in Model 2.

16. Notice the bond lengths in Model 3 are not shown as equal or similar. Explain why the hydroiodic acid molecule would have a longer bond length than the hydrofluoric acid molecule.

    Iodine is a much larger atom than fluorine. Therefore the bond length between iodine and hydrogen would be much longer than the bond length between fluorine and hydrogen.

17. Are bonds stronger or weaker when they are longer? Justify your reasoning using the principles of Coulombic attraction.

    Bonds are weaker when they are longer because the attraction between opposite charges decreases as distance increases.

18. According to the data in Model 3, how does the length of the bond between the hydrogen atom and the center atom of a binary acid affect the strength of the acid?

    As the bond length between the hydrogen and the center atom increases, the acid strength increases.

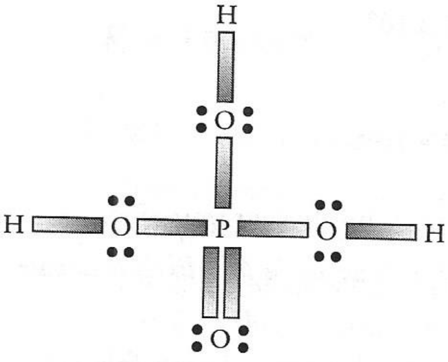
19. Which factor has more impact on the strength of an acid, the polarity of the bond or the length of the bond, when both are varied?

    Bond length has a greater influence on acid strength than bond polarity.

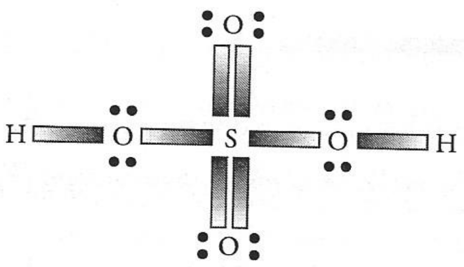
20. Predict which substance is more acidic: hydrosulfuric acid (H_2S) or hydroselenic acid (H_2Se). Explain your reasoning.

Hydroselenic acid would be a stronger acid than hydrosulfuric because the bond length between hydrogen and selenium would be longer due to the greater size of the selenium atom. ***Note:*** *at 25 °C, the* K_a *for* $H_2S = 1.0 \times 10^{-7}$ *and the* K_a *for* $H_2Se = 1.3 \times 10^{-4}$.

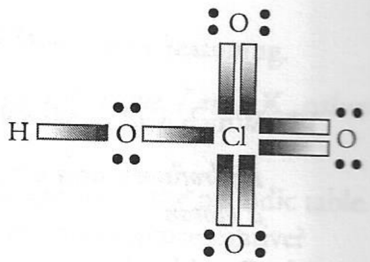
Model 4 – Comparing Oxo Acids



H_3PO_4
Phosphoric acid



H_2SO_4
Sulfuric acid



$HClO_4$
Perchloric acid

21. Refer to Model 4.

a. Write the names and chemical formulas for each acid below the structures shown.

See Model 4.

b. Why are these acids considered "oxo-acids"?

All of these acids contain at least one oxygen atom, and the acidic hydrogen is attached to the oxygen atom in the molecule.

22. Of the three center atoms in Model 4, which is most electronegative? Justify your reasoning.

The chlorine atom is the most electronegative. It is farthest to the right on the periodic table of the three and the bonds around the chlorine atom are the most polar, relative to the bonds around the other center atoms.

23. Even though the acidic hydrogen atoms are not bonded directly to the center atom in an oxo-acid, does the center atom affect the polarity of the O—H bond in oxo-acid molecules? Support your answer with evidence from Model 4.

Yes, the diagram in Model 4 shows that the polarity of the O—H bond does change when the center atom changes. The O—H bond is the most polar when it is in a molecule with a center atom that is more electronegative.

24. Based on what you have learned in Models 2 and 3, which acid in Model 4 is likely to be the strongest acid? Justify your reasoning.

Perchloric acid ($HClO_4$) is likely to be the strongest acid because the bond holding the acidic hydrogen is the most polar.

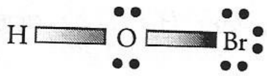
Read This!

Normally, when a bond is analyzed for polarity, it is only the electronegativity of the atoms on either end of the bond that are considered. In reality, however, a highly electronegative atom can affect a bond's polarity two or three bonds away. This effect is called the **inductive effect**.

25. Predict which substance would be more acidic, bromic acid ($HBrO_3$) or iodic acid (HIO_3). Explain your reasoning.

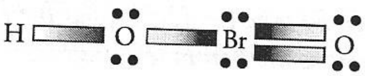
    Bromine is more electronegative than iodine. The bromine will have a stronger inductive effect on the polarity of the O—H bond. Therefore, bromic acid is likely to be stronger than iodic acid. ***Note:*** *the* K_a *for* $HBrO_3 = 1.0 \times 10^2$ *and the* K_a *for* $HIO_3 = 1.8 \times 10^{-1}$.

Model 5 – More Oxygen Atoms



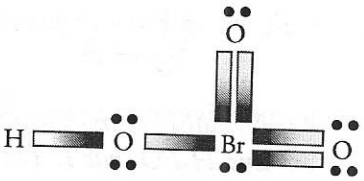
HBrO

Hypobromous acid



$HBrO_2$

Bromous acid



$HBrO_3$

Bromic acid

26. Write the names and chemical formulas for each acid under the structures shown in Model 5.

    See Model 5.

27. According to Model 5, how does the addition of oxygen atoms on the central atom of an oxo-acid affect the polarity of the O—H bond to the acidic hydrogen?

    When more oxygen atoms are attached to the center atom in an oxo-acid, the O—H bond increases in polarity. That is, its dipole moment increases.

28. Use the idea of the inductive effect to explain the changes in the polarity of the O—H bonds in Model 5.

    Oxygen is a highly electronegative atom. When more oxygen atoms are added to the molecule, the electrons in the entire molecule are attracted to the center atom by the inductive effect.

29. Which acid in Model 5 would you predict to be the strongest acid? Explain your reasoning.

    Bromic acid ($HBrO_3$) would be the strongest acid because it has the most oxygen atoms and the bond between the hydrogen and oxygen atoms is more polar than the O—H bonds in the other oxo-acids.

30. Chlorine makes four stable oxo-acids; hypochlorous acid, chlorous acid, chloric acid and perchloric acid. Match each acid with its acid dissociation constant (K_a) below.

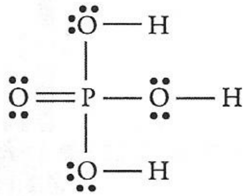
3.0×10^{-8}	1.1×10^{-2}	1.0×10^{-1}	1.0×10^{8}
Hypochlorous acid	*Chlorous acid*	*Chloric acid*	*Perchloric acid*
HClO	*$HClO_2$*	*$HClO_3$*	*$HClO_4$*

Extension Questions

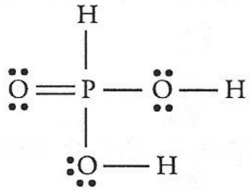
31. Sometimes the chemical formula of an acid can be misleading. Phosphoric acid (H_3PO_4) is a triprotic acid, but phosphorous acid (H_3PO_3) is a diprotic acid, and hypophosphorous acid (H_3PO_2) is a monoprotic acid.

    a. Draw Lewis dot-diagrams for each of these three acids. All of the structures include a double bonded oxygen. Consider carefully where the hydrogen atoms are positioned so that only the proper number would be acidic.

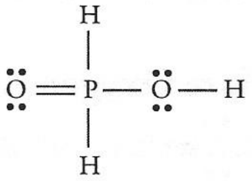
    Phosphoric acid

    Phosphorous acid

    Hypophosphorous acid

    Not all H atoms are acidic, or can be ionized. H_3PO_4 has three acidic protons, H_3PO_3 has two, and H_3PO_2 has 1. The acidic protons are bound to O atoms.

    b. Explain, using the concepts of molecular structure, why phosphorous acid and hypophosphorous acid are not triprotic acids.

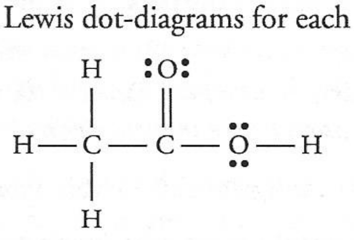
    Only the hydrogen atoms that are bonded to the highly electronegative oxygen atoms in the acid molecules will be donated in an acid–base reaction. The hydrogen atoms that are bonded directly to the phosphorous atoms will not be donated. The bonds between P and H are not polar and are stronger than the O—H bonds. The P—H bonds are strong enough to prevent ionization of the bonded H atoms.

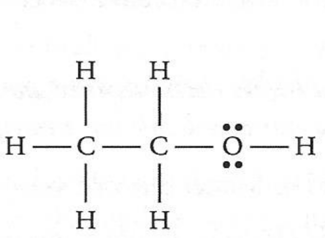
32. Consider the two substances below. One is an acid, and the other is classified as an alcohol.

    CH_3COOH
    Acetic acid

    CH_3CH_2OH
    Ethanol

    a. Draw Lewis dot-diagrams for each substance.

    b. Use the Internet to find the acid dissociation constant (K_a) for these two substances.

    Acetic acid $K_a = 1.7 \times 10^{-5}$

    Ethanol $K_a = 1.3 \times 10^{-16}$

    c. Explain why one is much more acidic than the other in terms of molecular structure.

    In the acetic acid molecule, the second oxygen will make the O—H bond more polar through the inductive effect. That will make it easier for the hydrogen to be donated in an acid–base reaction. The ethanol molecule does not have anything on the molecule that will increase the polarity of the O—H bond. That is, there is no inductive effect.

Teacher Resources – Strength of Acids

Learning Objectives

1. Relate the strength of an acid to the ease of breaking the bond between the hydrogen atom and the conjugate base.
2. Rank binary acids in order of strength by comparing the electronegativity of the conjugate bases or by comparing the length of the bond(s) between the hydrogen atom and the conjugate bases.
3. Rank oxo-acids in order of strength by comparing the electronegativity of the central atom or the number of oxygen atoms on the molecules.

Prerequisites

1. Students should be able to rank a set of acids from weakest to strongest when given the K_a values of the acids.
2. Students should understand acid–base reactions in terms of the Bronsted-Lowry definition, including being able to identify the conjugate base of an acid.
3. Students should be able to draw Lewis dot-diagrams for simple acid molecules, including oxo-acids.
4. Students should have a strong understanding of how electronegativity and distance affect the attractive forces that make a bond between atoms.

Assessment Questions

1. Which of the statements below would correctly explain why hydrochloric acid is a stronger acid than hydrofluoric acid?

   a. Fluorine has a larger electronegativity than chlorine.

   b. Fluorine has a smaller atomic radius than chlorine.

   c. Fluorine has fewer electrons than chlorine.

   d. Fluorine is higher on the periodic table than chlorine.

2. Which of the statements below would correctly explain why chloric acid is a stronger acid than sulfurous acid?

   a. Chlorine has a higher electronegativity than sulfur.

   b. Chlorine has a smaller atomic radius than sulfur.

   c. Chloric acid contains more oxygen atoms than sulfurous acid.

   d. Chloric acid contains longer bonds than those in sulfurous acid.

3. Describe the inductive effect for electronegativity and discuss how it influences the acidic nature of a hydrogen atom on an oxo-acid molecule.

Assessment Target Responses

1. *b*
2. *a*
3. *The electronegativity of the atoms in an acid affects the polarity of the bonds in the molecule. When the bond between the hydrogen and oxygen atom in an oxo-acid is more polar, the hydrogen tends to be more acidic, or more easily ionized. The polarity of the O–H bond can even be affected by the electronegativity of an atom one or two bonds away in the molecule. This is the inductive effect.*

Alignment with AP Chemistry Framework

- **Essential Knowledge 2.A.1:** The different properties of solids and liquids can be explained by differences in their structures, both at the particulate level and in their supramolecular structures.

  Learning Objective 2.2 The student is able to explain the relative strengths of acids and bases based on molecular structure, interparticle forces, and solution equilibrium.

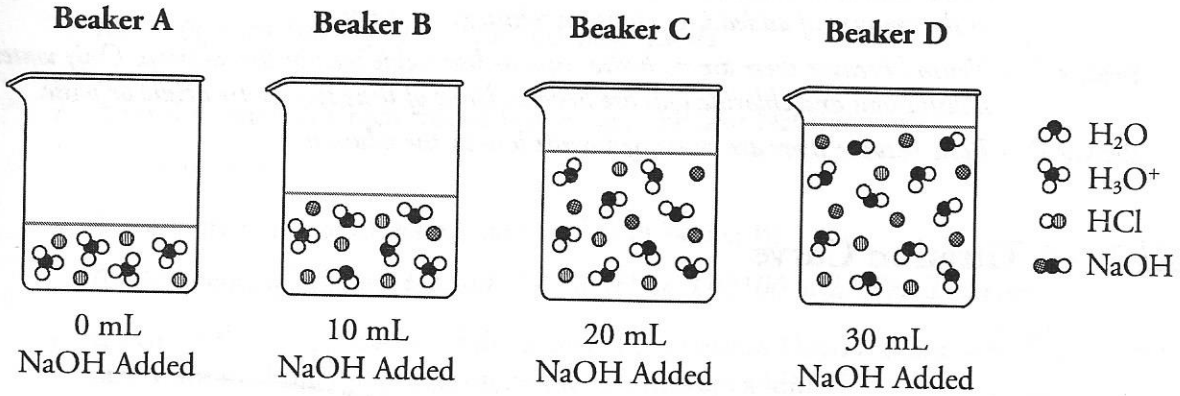
Titration Curves

What is in the beaker at each stage of a titration?

Why?

Titration is a very useful technique for determining the properties of an unknown solution. The unknown is reacted with a known titrant solution by adding small volumes until an equivalence point is reached. Titrations can be done using an acid–base reaction, redox reaction or precipitation. Most commonly it is used to find the concentration of a solute. Depending on the type of reaction used, a chemist might also be able to determine the strength of an unknown acid or base, the potential of a species to oxidize or reduce another species, or the solubility of a substance. This activity will focus on an acid–base titration.

Model 1 – HCl Sample Titrated with NaOH



Beaker	A	B	C	D
H_2O molecules	0	*4*	*8*	*8*
H_3O^{1+} ions	4	*2*	*0*	*0*
Cl^{1-} ions	4	*4*	*4*	*4*
Na^{1+} ions	0	*2*	*4*	*6*
OH^{1-} ions	0	*0*	*0*	*2*

1. Consider the diagrams in Model 1.
   a. Which beaker illustrates the solution before the titration begins?
   Beaker A illustrates the solution before any NaOH has been added.
   b. Why does the volume increase from Beaker A to Beaker D?
   The volume in the beaker increases because NaOH solution has been added.
2. Explain why there are no HCl molecules in any of the beakers.
   Hydrochloric acid is a strong acid—it fully ionizes in water.
3. Write a balanced net ionic equation for the reaction between HCl and NaOH during the titration.
   $H^{1+}(aq) + OH^{1-}(aq) \rightarrow H_2O(l)$

4. Which species in the illustrations in Model 1 are simply spectator ions?

   The chloride ions (Cl^{1-}) and the sodium ions (Na^{1+}) are spectator ions.

5. Complete the table in Model 1 by counting the number of each species in each of the four beakers. Record the numbers in the appropriate box in the table. The first column has been done for you as an example.

   See Model 1.

6. For each beaker in Model 1 determine if the solution would be acidic, basic or neutral when checked with a pH meter. Justify your reasoning.

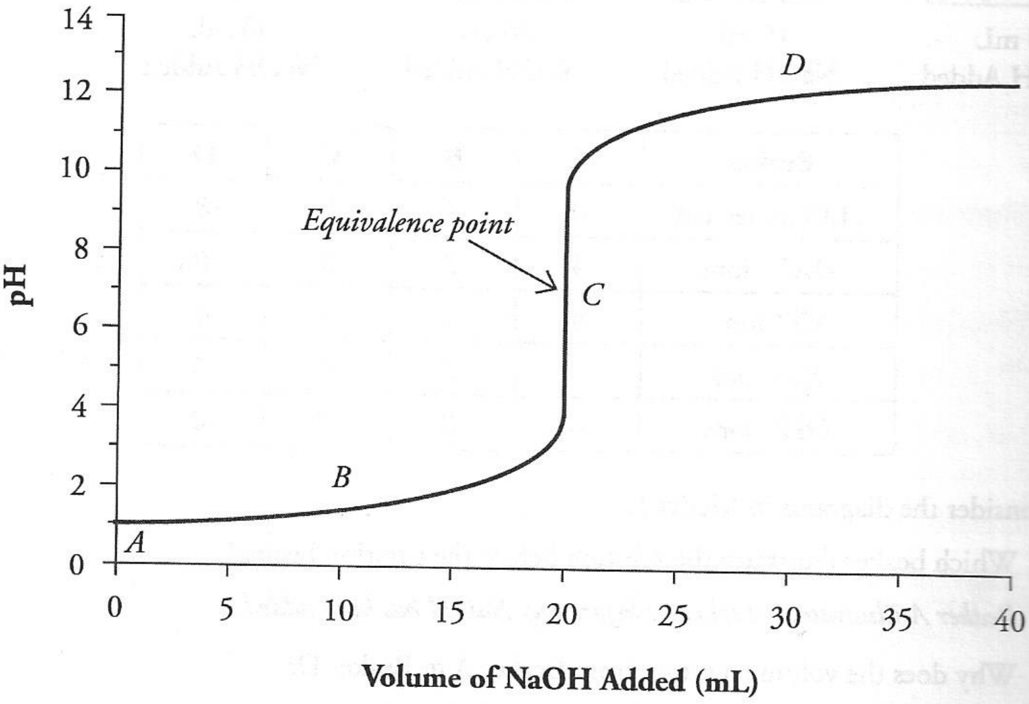
   Beaker A – *Acidic because the HCl has fully ionized and formed hydronium ions in the solution. There is an excess of hydronium ions in solution.*

   Beaker B – *Acidic because only some of the hydronium ions have reacted with NaOH. Some hydronium ions remain in solution. There is still an excess of hydronium ions, relative to the amount of added OH$^-$ ions, in solution.*

   Beaker C – *Neutral because there are no hydronium or hydroxide ions in the solution. Only water, sodium ions and chloride ions are present. None of these species are acidic or basic.*

   Beaker D – *Basic because there are excess hydroxide ions in the solution.*

Model 2 – A Titration Curve



7. The graph in Model 2 shows the pH of the resulting solution from the titration illustrated in Model 1. Label four points on the graph in Model 2 to correspond with the four beakers in Model 1.

   See Model 2.

8. The sample for the titration shown in Models 1 and 2 was 20.00 mL of 0.100 M hydrochloric acid. Verify that the initial pH of this sample is correctly plotted in the graph in Model 2. Show a calculation to support your answer.

   $pH = -log\,(0.100)$

   $pH = 1.000$

9. The solution in Beaker B of Model 1 was the result of 10.00 mL of 0.100 M sodium hydroxide solution being added to Beaker A.

   a. How many moles of HCl were initially in Beaker A?

   $$(0.02000\ L)(0.100\,\frac{mole}{L}) = 0.00200\ mole\ HCl$$

   b. How many moles of NaOH were added to Beaker A to get Beaker B?

   $$(0.01000\ L)(0.100\,\frac{mole}{L}) = 0.00100\ mole\ NaOH$$

   c. After the reaction, which species is in excess –HCl or NaOH?

   HCl is in excess.

   d. How many moles of excess reactant are left in Beaker B?

   0.00100 mole of HCl reacted with the NaOH, so 0.00100 mole of HCl remains.

   e. Calculate the concentration of the excess HCl or excess NaOH. Make sure to consider the new volume of the solution (assume the volumes are additive).

   $$\frac{0.00100\ mole}{0.02000\ L + 0.0100\ L} = 0.0333\ M\ NaOH$$

   f. Verify the pH of Beaker B in the graph in Model 2. Show a calculation to support your answer.

   STOP

   $pH = -log(0.0333) = 1.477$

10. The solution in Beaker C of Model 1 was the result of 20.00 mL of 0.100 M sodium hydroxide solution being added to Beaker A.

    a. How many moles of HCl were initially in Beaker A?

    $$(0.02000\ L)(0.100\,\frac{mole}{L}) = 0.00200\ mole\ HCl$$

    b. How many moles of NaOH were added to Beaker A to get Beaker C?

    $$(0.02000\ L)(0.100\,\frac{mole}{L}) = 0.00200\ mole\ NaOH$$

    c. After the reaction, which species is in excess –HCl or NaOH?

    Neither HCl nor NaOH is in excess. There have been equal moles of each added.

    d. Verify the pH of Beaker C in the graph in Model 2.

    The pH of Beaker C is 7.000 because only water, sodium ions and chloride ions remain in the solution.

11. The solution in Beaker D of Model 1 was the result of 30.00 mL of 0.100 M sodium hydroxide solution being added to Beaker A.

    a. How many moles of HCl were initially in Beaker A?

    $$(0.02000\ L)(0.100\ \frac{mole}{L}) = 0.00200\ mole\ HCl$$

    b. How many moles of NaOH were added to Beaker A to get Beaker D?

    $$(0.03000\ L)(0.100\ \frac{mole}{L}) = 0.00300\ mole\ NaOH$$

    c. After the reaction, which species is in excess –HCl or NaOH?

    NaOH is in excess.

    d. How many moles of excess reactant are left in Beaker D?

    0.00200 mole of NaOH reacted with HCl, so 0.00100 mole of NaOH remains.

    e. Calculate the concentration of the excess HCl or excess NaOH. Make sure to consider the new volume of the solution (assume the volumes are additive).

    $$\frac{0.00100\ mole}{0.02000\ L + 0.0300\ L} = 0.0200\ M\ NaOH$$

    f. Verify the pH of Beaker D in the graph in Model 2. Show a calculation to support your answer.

    $pOH = -log(0.0200) = 1.699$

    $pH = 14 - 1.699 = 12.301$

12. The point on the graph in Model 2 corresponding to Beaker C is called the **equivalence point.**

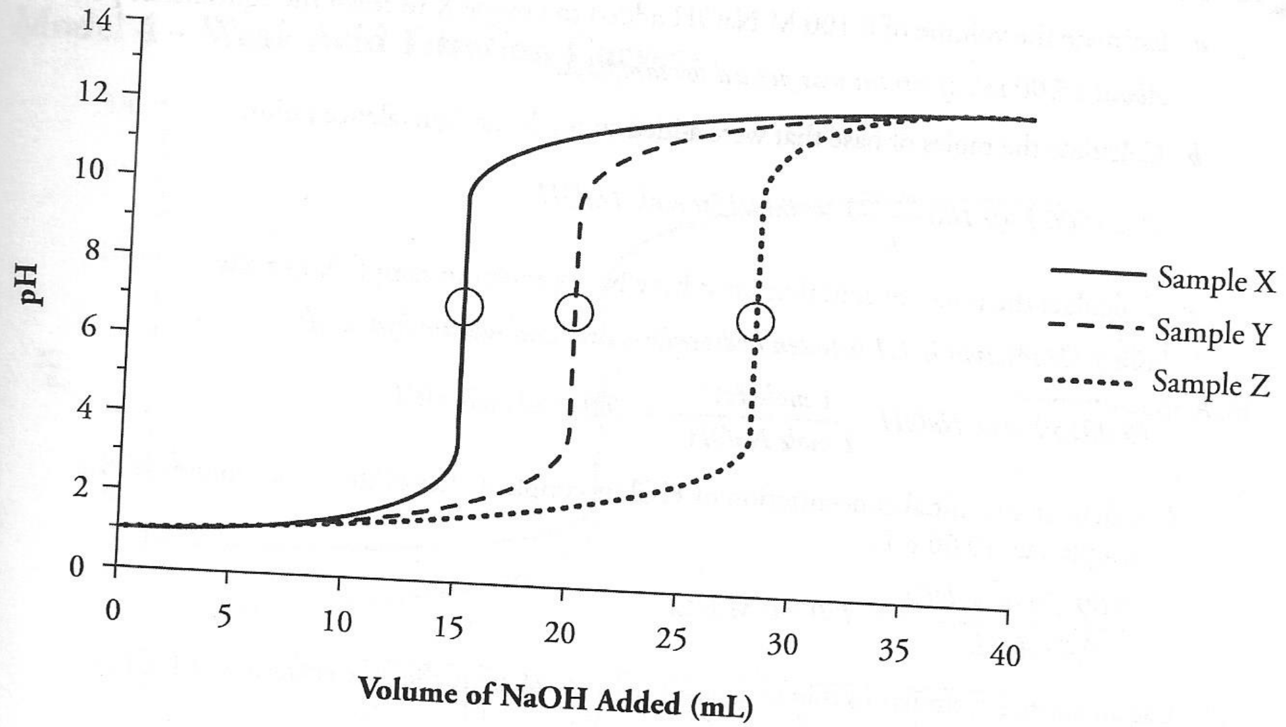
    a. Label the equivalence point on the graph in Model 2.

    See Model 2.

    b. With your group, discuss why this point might be called the "equivalence point." Be prepared to share your thoughts with the class.

    The point on the graph that represents Beaker C (see Model 2) is the equivalence point because that is when the moles of hydrochloric acid and the moles of sodium hydroxide are equal. Any point beyond the equivalence point is just an addition of excess sodium hydroxide.

Model 3 – Determining the Unknown Concentration



13. The graph in Model 3 shows the titration curves of three samples of hydrochloric acid, each having the same volume (20.00 mL) but different concentrations. All three samples were titrated with the same sodium hydroxide solution. What feature of the titration curve changes the most when samples with different concentrations are titrated?

    The feature that changes the most is the volume of sodium hydroxide needed to reach the equivalence point.

14. Does changing the concentration of the sample have a significant effect on the initial or final pH for the titration curve?

    No, the pH of the three samples is very similar in those regions.

15. Circle the equivalence point of each titration in Model 3. Notice that the pH at all three equivalence points is 7.00. Explain how this can be the case even though the initial samples were different concentrations.

    The equivalence points of all three reactions have a pH of 7.00 (see Model 2) because in all three cases the only species in the beaker at that point is water, sodium ions and chloride ions. By definition the "equivalence point" is the point where the hydrochloric acid and sodium hydroxide have reacted in stoichiometric amounts, so neither is present in solution once the reaction is complete.

16. Refer to Model 3.

   a. Estimate the volume of 0.100 M NaOH added to sample X to reach the equivalence point.

   About 15.00 mL of titrant was needed for sample X.

   b. Calculate the moles of base that were added to reach the equivalence point.

   $$(0.01500\ L)(0.100\ \frac{mole}{L}) = 0.00150\ mole\ NaOH$$

   c. Calculate the moles of acid that must have been present in sample X initially.

   Since the reaction is 1:1 between hydrochloric acid and sodium hydroxide:

   $$(0.00150\ mole\ NaOH\ \frac{1\ mole\ HCl}{1\ mole\ NaOH} = 0.00150\ mole\ HCl$$

   d. Calculate the initial concentration of HCl in sample X. Recall the initial volume of the sample was 20.00 mL.

   $$\frac{0.00150\ mole\ HCl}{0.02000\ L} = 0.0750\ M\ HCl$$

17. Use an approach similar to that in Question 16 to calculate the concentration of HCl in sample Z before the titration.

   About 28.00 mL of NaOH was needed to reach the equivalence point for sample Z.

   $$(0.02800\ L)(0.100\ \frac{mole}{L}) = 0.00280\ mole\ NaOH$$

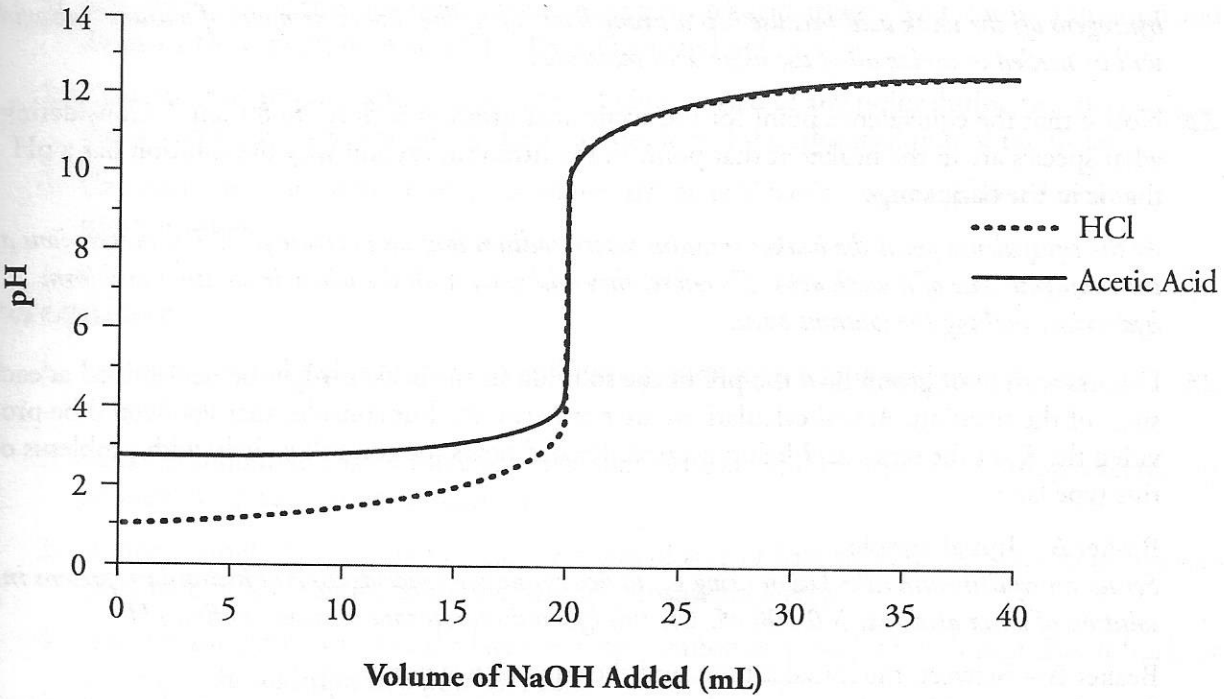
   $$(0.00280\ mole\ NaOH\ \frac{1\ mole\ HCl}{1\ mole\ NaOH} = 0.00280\ mole\ HCl$$

   $$\frac{0.00280\ mole\ HCl}{0.02000\ L} = 0.140\ M\ HCl$$

STOP

Extension Questions

Model 4 – Weak Acid Titration Curves



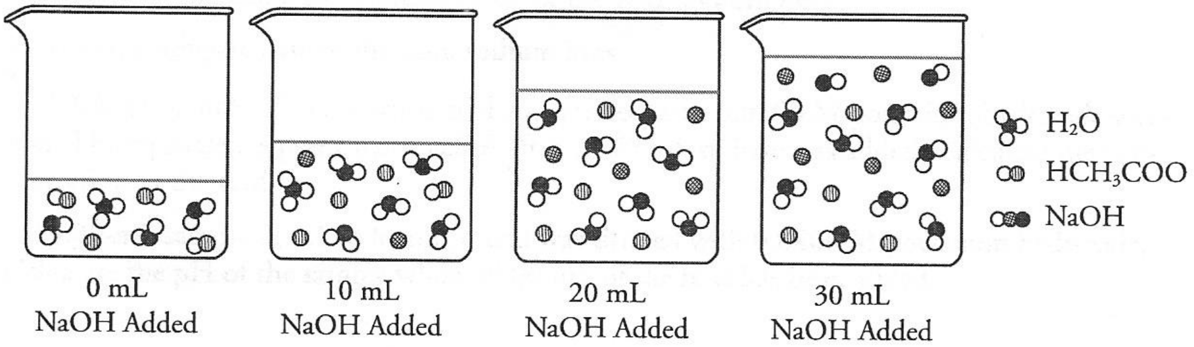
18. Consider Model 4. The two titration curves were produced using the same volume (20.00 mL) and concentration of acid (0.100 M). The titrant was 0.100 M NaOH. What is the major difference in the shape of a titration curve for a weak acid compared to the curve for a strong acid?

The major difference is the initial pH. Because the acetic acid is weak, the pH of the HCl solution is much lower, even though the concentrations of the acid solutions are equal.

19. Write the net ionic equation for acetic acid (HCH_3COO) with sodium hydroxide.

$HCH_3COO(aq) + OH^{1-}(aq) \rightarrow H_2O(l) + CH_3COO^{1-}(aq)$

20. Draw a particulate representation of the weak acid titration at each of the four stages. Refer to Model 1 as a guide, but think about how a weak acid would be different from a strong acid.



21. Notice that the same volume of NaOH is required to reach the equivalence point for both the strong and weak acid. Explain why this is the case.

    Although the acid is weak and does not initially ionize all of the hydrogen ions, the moles of acid present are the same regardless of being a weak or strong acid. The sodium hydroxide will "pull" the hydrogens off the weak acid because it is a strong base. Therefore, the same moles of sodium hydroxide will be needed to ionize all of the weak acid molecules.

22. Notice that the equivalence point for the acetic acid titration is closer to 8 than 7. Considering what species are in the beaker at that point in the titration, explain why the solution has a pH that is in the basic range.

    At the equivalence point the beaker contains water, sodium ions and acetate ions. The acetate ions are the conjugate base of a weak acid. Therefore, they will react with the water in solution and form hydroxide, making the solution basic.

23. Discuss with your group how the pH of the solution in the beaker might be determined at each stage of the titration. Actual calculations are not necessary, but consider that you would be provided the K_a of the weak acid being titrated. Record notes for yourself to help with problems of this type later.

    Beaker A – Initial sample
    Set up an equilibrium calculation using K_a *to determine the concentration of hydronium present in a solution of weak acid that is 0.100 M. Use this hydronium ion concentration to find pH.*

    Beaker B – Between the initial sample and the equivalence point
    Both the weak acid and its conjugate base are present in the solution, therefore, a buffer exists. Set up an equilibrium calculation using K_a*, the concentration of unreacted weak acid, and the concentration of conjugate base already made. Find the hydronium ion concentration and use it to calculate pH.*

    Beaker C – At the equivalence point
    Use K_a *and* K_w *to determine* K_b *for the conjugate base. Calculate the diluted concentration of the conjugate base (considering the amount of titrant added). Set up an equilibrium calculation using* K_b *to determine the hydroxide concentration when the conjugate base concentration is at that diluted concentration. Use the hydroxide concentration to find pOH and then pH.*

    Beaker D – Beyond the equivalence point
    Determine the moles of excess sodium hydroxide and calculate a molarity using the total volume of the solution. Use this hydroxide concentration to find pOH and then pH.

Teacher Resources – Titration Curves

Learning Objectives

1. Describe the contents of a beaker containing a strong acid at any point during a titration and discuss why it might have an acidic, basic or neutral pH.
2. Calculate the pH for a strong acid sample being titrated at any point during the titration given the concentration and volume of the acid sample and the concentration of the titrant.
3. Calculate the concentration of an unknown strong acid based on data gathered from a titration curve.

Prerequisites

1. Students should be able to write a net ionic equation for a strong acid reacting with a strong base.
2. Students should be able to calculate the moles of excess acid or base in a limiting reactant type problem for a neutralization reaction.
3. Students should be able to calculate the moles of acid or base that are necessary to neutralize a given base or acid sample using the concepts of stoichiometry.
4. Students should be able to calculate the concentration of a species in solution after it has been diluted by the addition of a new solution.
5. Students should be able to calculate the pH of a strong acid solution.
6. Students should have seen at least a demonstration of a titration and be aware of the terms analyte and titrant.

Assessment Questions

1. Which of the following best describes the contents of the sample beaker at the equivalence point of a strong acid titration using sodium hydroxide as the titrant?
   a. Water, hydronium ions, conjugate base of the acid.

   b. Water, hydroxide ions, conjugate base of the acid.

   c. Water, hydronium ions, conjugate base of the acid, sodium ions.

   d. Water, conjugate base of the acid, sodium ions.
2. A 25.00-mL sample of monoprotic acid was titrated with 0.0800 M potassium hydroxide solution. The equivalence point was reached after 18.75 mL of base was added. Calculate the concentration of the acid.
3. A 15.00-mL sample of 0.120 M nitric acid was titrated with 0.0800 M potassium hydroxide. Calculate the pH of the sample when 10.00 mL of the base has been added.

Assessment Target Responses

1. *d*
2. *0.0600 M*
3. *pH = 1.398*

Teacher Tips

- Before working through this activity, students should have at least seen a demonstration of a titration. The questions will be more in context if they have seen a buret with a stopcock that can slowly add titrant to the unknown solution.
- Because teachers may introduce titration concepts at different times during the year, the discussion of weak acid titration was limited to the *Extension Questions*.
- Note that the particulate diagrams in Model 1 are over-simplified to help students focus on the acid–base reaction ocurring in the beaker. It is worth noting with students that beaker C would contain some hydronium and hydroxide ions (1×10^{-7} M).

Alignment with AP Chemistry Framework

- **Essential Knowledge 1.E.2:** Conservation of atoms makes it possible to compute the masses of substances involved in physical and chemical processes. Chemical processes result in the formation of new substances, and the amount of these depends on the number and the types and masses of elements in the reactants, as well as the efficiency of the transformation.

  Learning Objective 1.20 The student can design, and/or interpret data from an experiment that uses titration to determine the concentration of an analyte in a solution.

- **Essential Knowledge 3.A.2:** Quantitative information can be derived from stoichiometric calculations that utilize the mole ratios from the balanced chemical equations. The role of stoichiometry in real-world applications is important to note, so that it does not seem to be simply an exercise done only by chemists.
- **Essential Knowledge 6.C.1:** Chemical equilibrium reasoning can be used to describe the proton-transfer reactions of acid–base chemistry.

  Learning Objective 6.13 The student can interpret titration data for monoprotic or polyprotic acids involving titration of a weak or strong acid by a strong base (or a weak or strong base by a strong acid) to determine the concentration of the titrant and the pK_a for a weak acid, or the pK_b for a weak base.

Polyprotic Acids

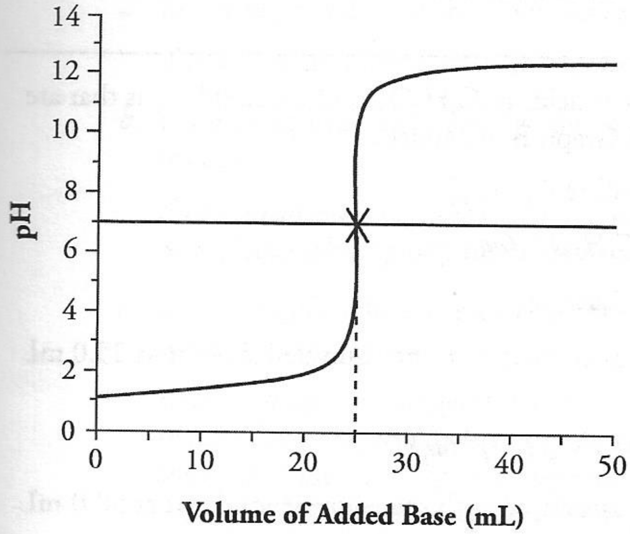
What can a titration curve tell us about polyprotic acids?

Why?

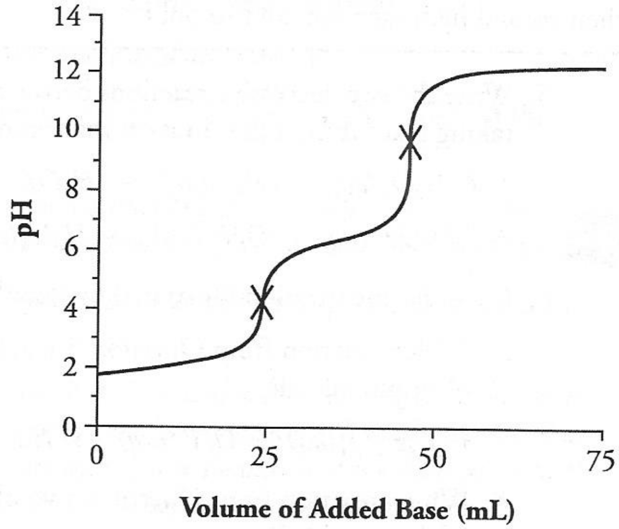
The graph commonly known as a titration curve for an acid (pH of the solution versus the volume of base added) can give us some valuable information about the acid. You can calculate the concentration of the acid and find its acid dissociation constant (K_a) if it is a weak acid. There are many acids, however, that do not produce a typical titration curve. These acids are polyprotic, meaning they contain more than one acidic hydrogen.

Model 1 – Titration of a Monoprotic and Diprotic Acid

Graph A. 25-mL Sample of Hydrochloric Acid Titrated with 0.100 M NaOH



Graph B. 25-mL Sample of Maleic Acid Titrated with 0.100 M NaOH



1. Examine the titration curves in Model 1.
   a. Identify the analyte and titrant that reacted to produce graph A.

      Analyte *Hydrochloric acid* Titrant *Sodium hydroxide, 0.100 M*

   b. Identify the analyte and titrant that reacted to produce graph B.

      Analyte *Maleic acid* Titrant *Sodium hydroxide, 0.100 M*

2. Which acid in Model 1 is a monoprotic acid and which is a diprotic acid? *Hint:* What do the prefixes mono- and di- mean?

   Hydrochloric acid is monoprotic and maleic acid is diprotic.

3. Place an X on the equivalence point of the titration for graph A. What is equal when this titration is at the equivalence point?

   At the equivalence point of the titration, the reaction is stoichiometrically complete. In the case of graph A where the reaction has a 1:1 ratio between acid and base, the moles of hydrochloric acid are equal to the moles of sodium hydroxide.

4. Examine the titration curve for the diprotic acid. How many equivalence points are there? Place an X on each equivalence point.

   There are two equivalence points. See Model 1.

Read This!

When polyprotic acids react with hydroxide ions (or any other base) in solution, hydrogen ions are donated one at a time. The first acidic proton reacts with the base (OH^{1-}) like this:

$$H_2A + OH^{1-} \longleftrightarrow H_2O + HA^{1-}$$

When all of the acid molecules have donated their first hydrogen ion (proton), they will begin to donate the second hydrogen ion if there is still base present.

$$HA^{1-} + OH^{1-} \longleftrightarrow H_2O + A^{2-}$$

If a third acidic hydrogen is present, it will only be donated once all of the acid molecules have donated their second hydrogen ion, and so on.

5. Write the two successive reactions between maleic acid, $H_2C_4H_2O_4$, and hydroxide ions that are taking place during the titration that produced Graph B of Model 1.

   $H_2C_4H_2O_4(aq) + OH^{1-}(aq) \rightarrow H_2O(l) + HC_4H_2O_4^{1-}(aq)$

   $HC_4H_2O_4^{1-}(aq) + OH^{1-}(aq) \rightarrow H_2O(l) + C_4H_2O_4^{2-}(aq)$

6. Consider the titration illustrated by Graph B of Model 1.

   a. Which reaction from Question 5 would be associated with the equivalence point at 25.0 mL of titrant added?

   $H_2C_4H_2O_4(aq) + OH^{1-}(aq) \rightarrow H_2O(l) + HC_4H_2O_4^{1-}(aq)$

   b. Which reaction from Question 5 would be associated with the equivalence point at 50.0 mL of titrant added?

   $HC_4H_2O_4^{1-}(aq) + OH^{1-}(aq) \rightarrow H_2O(l) + C_4H_2O_4^{2-}(aq)$

7. Use the information in Model 1 to calculate the concentration of the hydrochloric acid sample that was titrated to produce the monoprotic acid titration curve.

   (25.0 mL base)(0.100 M base) = (25.0 mL acid)([HCl])

   [HCl] = 0.100 M

8. Notice in Model 1 that the volume of titrant needed for the second equivalence point of the diprotic acid is double that needed for the first equivalence point. Propose an explanation for why that is the case.

   25.0 mL of titrant was needed to react with all the acid molecules for the first reaction. That is, 25.0 mL of 0.100 M NaOH is needed to neutralize the first acidic proton in its entirety. An additional 25.0 mL of 0.100 M NaOH is needed to neutralize the second acidic proton. There are equal moles of the first and second acidic protons, and so equal volumes (moles) of OH^{1-} *are needed to neutralize both.*

9. Use the information in Model 1 to calculate the concentration of the maleic acid sample that was titrated to produce the diprotic acid titration curve.

   (25.0 mL base)(0.100 M base) = *(25.0 mL acid)*$([H_2C_4H_2O_4])$

   $[H_2C_4H_2O_4]$ = *0.100 M*

10. The pH of the equivalence point in Graph A of Model 1 was 7.00.

    a. State the major species that were in solution at that point in the titration.

    At the equivalence point, the solution contained water and sodium chloride salt.

    b. Explain why the pH was neutral at the equivalence point.

    Water and sodium chloride salt are both neutral species. At the equivalence point, the solution contained equal moles of H^+ *and* OH^- *ions.*

11. Consider Graph B in Model 1.

    a. Estimate pH values at the equivalence points for the diprotic acid titration.

    The pH values at the equivalence points for the diprotic acid are 4 and 9.

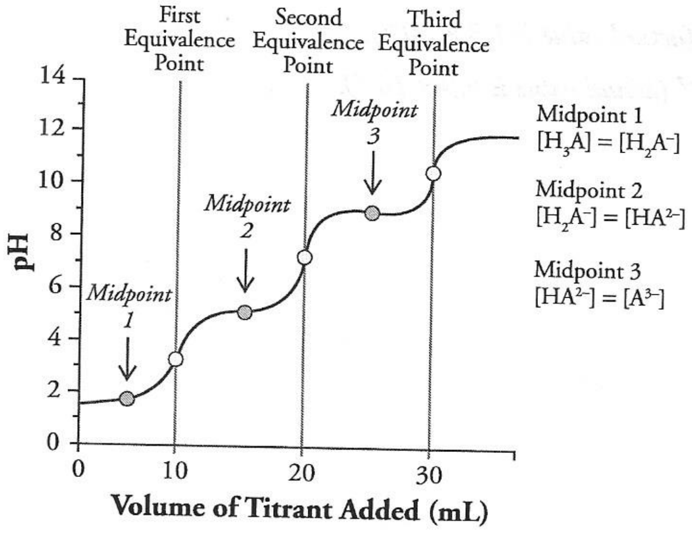
    b. For each equivalence point, list the major species present in solution at that point of the titration.

    First equivalence point: the solution contains predominantly $HC_4H_2O_4^{1-}$ *ions,* Na^{1+} *ions and water.*
    Second equivalence point: the solution contains predominantly $C_4H_2O_4^{2-}$ *ions,* Na^{1+} *ions and water.*

    c. Justify the pH values at each equivalence point based on what major species are present in solution at the time.

    At the first equivalence point, the $HC_4H_2O_4^{1-}$ *ion is still an acid so it is reacting with the water in the solution to form hydronium. Thus, the solution still has an acidic pH. At the second equivalence point, the* $C_4H_2O_4^{2-}$ *no longer has an acidic hydrogen to donate, so it is a base and will take some hydrogen ions from water to form hydroxide ions. Thus, the solution has a basic pH.*

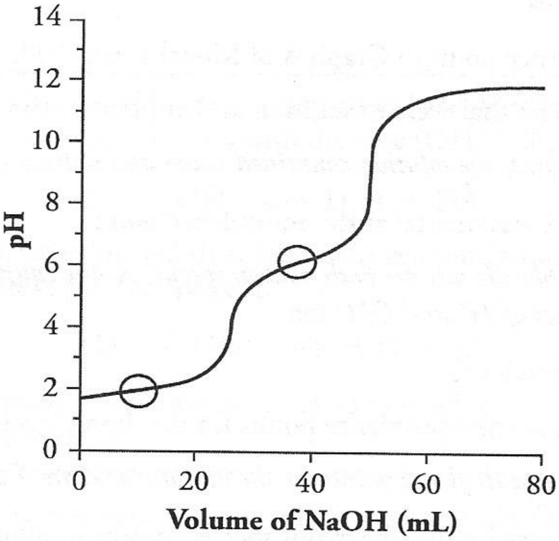
12. Sketch a graph similar to those in Model 1 for a triprotic acid like citric acid, $H_3C_6H_5O_7$. The concentration of the acid was 0.16 M and the sodium hydroxide titrant was 0.10 M. Consider the approximate pH's and volumes of titrant that would be appropriate for each equivalence point.



Note: *Students are not expected to have accurate pH values on this graph. It is only a sketch. What is important is that students can calculate the volume of titrant needed to reach the 1st, 2nd and 3rd endpoints, and that they can predict the first two endpoints will be in the acidic range while the final endpoint will be in the basic range. It is also important to note that this is an idealized curve. In reality there are no common triprotic acids that will give such a clean curve in the lab.*

Extension Questions

Model 2 – Maleic Acid



13. The titration curve for a weak monoprotic acid with a strong base can be used to determine the K_a of the weak acid. Describe how this is done.

    The pH at the point that is halfway to the equivalence point is equal to the pK_a *of the acid. This pH value can be read off the titration curve.*

14. The titration curve for a weak diprotic acid with a strong base can also be used to determine both the K_{a1} and K_{a2} of the diprotic acid. Consider the titration curve for maleic acid in Model 2.

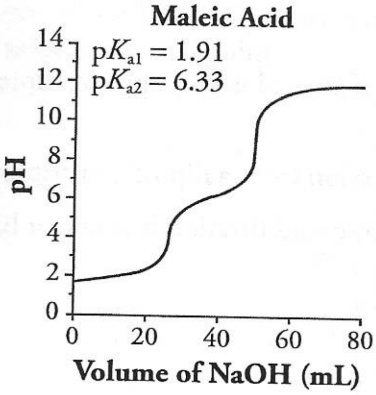
    a. Circle two points on the graph in Model 2 that could be used to find K_{a1} and K_{a2} for maleic acid.

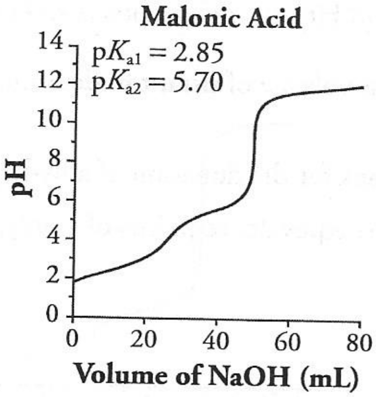
    See Model 2. The two points circled are halfway to the first and second equivalence points, respectively.

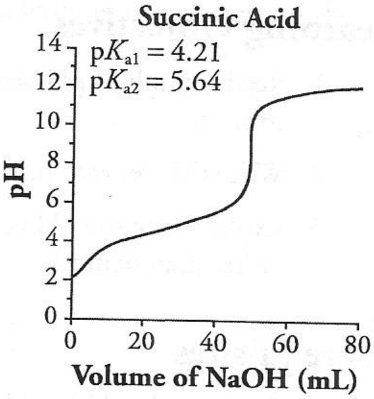
    b. Estimate the K_{a1} and K_{a2} of maleic acid.

    $pK_{a1} = 2$, *so* $K_{a1} = 1.0 \times 10^{-2}$ *(actual value is* 1.3×10^{-2}*).*
    $pK_{a2} = 6.2$, *so* $K_{a2} = 6.3 \times 10^{-7}$ *(actual value is* 5.9×10^{-7}*).*

15. Consider the titration curves for the three diprotic acids below. All three acids were titrated using the same titrant solution.







a. Were all three diprotic acids at the same concentration when they were titrated? Justify your reasoning.

Yes. The second equivalence point occurred at the same volume of titrant for all three acids, so their concentrations must be the same.

b. Propose an explanation for why the titration curve for succinic acid appears to be that of a monoprotic acid.

The two K_a values are very close together. The reactions do not happen one at a time; they occur closer together so a titration curve does not show two distinct equivalence points.

Teacher Resources – Polyprotic Acids

Learning Objectives

1. Read a graph of pH versus volume of titrant to determine if an acid is monoprotic, diprotic or triprotic.
2. Write the stepwise reactions for the donation of a hydrogen ion from a diprotic or triprotic acid.
3. Explain why the pH at the equivalence points of a polyprotic acid titration is acidic or basic rather than neutral.

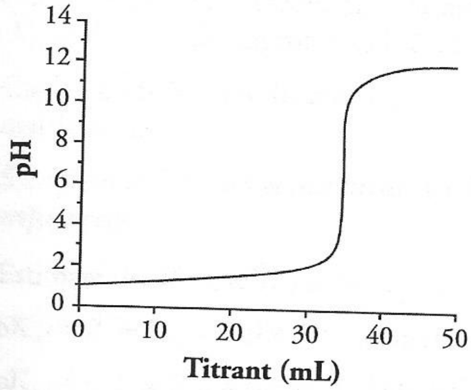
Prerequisites

1. Students should be able identify the equivalence point on a graph of pH versus volume of titrant for a strong or weak acid reacting with strong base.
2. Students should be able to write acid dissociation reactions for strong or weak acids.
3. Students should be able to identify the major species in solution at any point during an acid–base titration.
4. Students should be able to justify the pH of the solution at any point during an acid–base titration based on the major species in solution at that point.

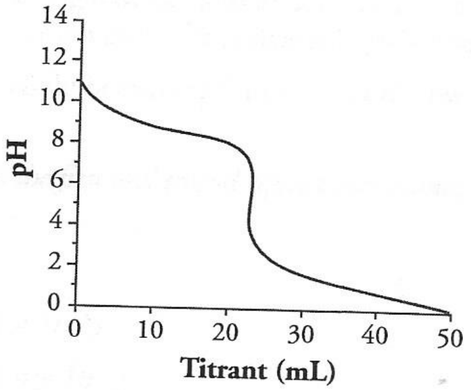
Assessment Questions

1. Which graph below illustrates a pH titration curve between a diprotic acid and a base?

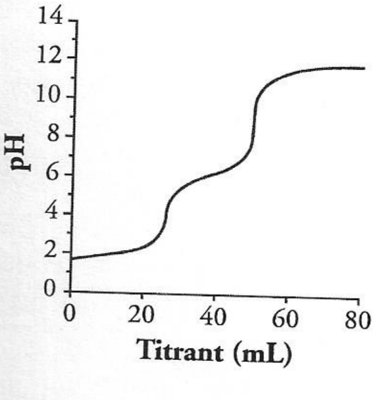
a.



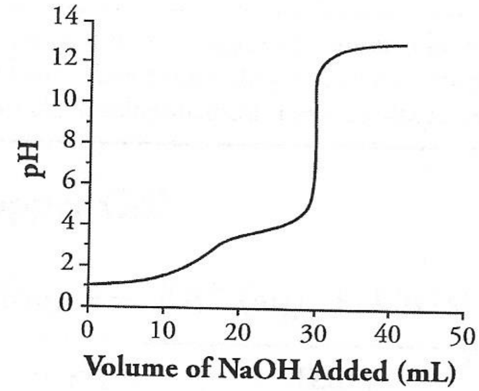
c.



b.



2. Write the acid dissociation reactions for the diprotic acid phosphorous acid, H_3PO_3.
3. Consider the titration curve below for the titration of oxalic acid, $H_2C_2O_4$ and sodium hydroxide. Identify the two equivalence points, and explain the pH by describing the contents of the solution at each point.



Assessment Target Responses

1. *b*
2. $H_3PO_3(aq) + H_2O(l) \longleftrightarrow H_3O^{1+}(aq) + H_2PO_3^{1-}(aq)$

   $H_2PO_3^{1-}(aq) + H_2O(l) \longleftrightarrow H_3O^{1+}(aq) + HPO_3^{2-}(aq)$
3. *The equivalence points in the titration between oxalic acid and sodium hydroxide occur at a pH of 3 and 8. At the first equivalence point, the solution contains* $HC_2O_4^{1-}$. *Since there is a second acidic hydrogen on this species, the pH of the first equivalence point is acidic. At the second equivalence point, the solution contains* $C_2O_4^{2-}$. *This species is a base, so the second equivalence point is basic because* $C_2O_4^{2-}$ *accepts a proton from* H_2O *to produce* OH^-.

Teacher Tips

- This activity could be accompanied by a lab experience where students titrate a diprotic acid and measure the pH along the way. The lab could either take place after doing this activity or before.
- The graphs in this activity are idealized for educational purposes. Many polyprotic acids produce ambiguous results where the equivalence points are subtle at best.

Alignment with AP Chemistry Framework

- **Essential Knowledge 6.C.1:** Chemical equilibrium reasoning can be used to describe the proton-transfer reactions of acid–base chemistry.

  Learning Objective 6.13 The student can interpret titration data for monoprotic or polyprotic acids involving titration of a weak or strong acid by a strong base (or a weak or strong base by a strong acid) to determine the concentration of the titrant and the pK_a for a weak acid, or the pK_b for a weak base.

Electrochemical Cell Voltage

How do changes in concentration within a cell change the voltage of the cell?

Why?

Batteries are simply electrochemical cells in a compact container. The most common are sold as 9-volt or 1.5-volt, but are these voltages reliable? Does the voltage of an electrochemical cell stay constant as the cell runs towards equilibrium? Can an electrochemical cell have a voltage other than its standard voltage?

Model 1 – Zinc and Copper Cell

$$\mathbf{Zn\,(s) + Cu^{2+}\,(aq) \leftrightarrow Zn^{2+}\,(aq) + Cu\,(s) \quad E^\circ = 1.100\ V}$$

Time (min)	**[Cu^{2+}] (M)**	**[Zn^{2+}] (M)**	**Voltage (V)**
1	1.750	0.250	1.123
2	1.500	0.500	1.113
3	1.250	0.750	1.106
4	1.000	1.000	1.100
5	0.750	1.250	1.094
6	0.500	1.500	1.087
7	0.250	1.750	1.077

1. Is the cell in Model 1 spontaneous or not? Use evidence from Model 1 to justify your answer.

   Yes, the cell is spontaneous. The standard voltage, and all of the voltages in the table, are positive.

2. Is the reaction in Model 1 favoring the reverse direction at any point during the experiment? Justify your answer.

   No, all of the voltages in the Model 1 are positive, so the reaction is always running in the forward direction.

3. Refer to Model 1.

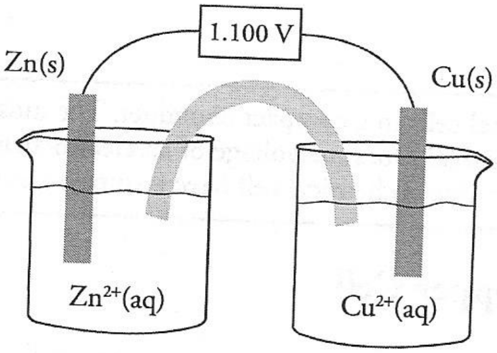
   a. What is the standard cell potential for the reaction between zinc and copper?

   $E^\circ = 1.100\ V$

   b. What are the concentrations of the zinc and copper solutions when the standard cell potential is obtained?

   The zinc and copper solutions are both 1.00 M when a voltage of 1.100 V is obtained.

4. Sketch how the Zn^{2+}(aq)/Cu (s) electrochemical cell in Model 1 may appear in a lab setup. Label the electrodes and solutions. Include a voltmeter in your drawing.



5. Is the reaction in Model 1 at equilibrium at any point during the experiment? If no, in which direction must the reaction proceed to reach equilibrium?

   No, the reaction is never at equilibrium. At equilibrium the voltage would be zero. The reaction must continue to run in the forward direction to reach equilibrium.

6. According to the data in Model 1, does an electrochemical cell provide a constant voltage as it proceeds?

   No, as the cell runs the voltage goes down.

7. Would you expect a 9-V battery to always provide 9 V? Justify your reasoning.

   No, a 9-V battery may start at 9 V, but as it runs, the voltage will decrease until it goes "dead" upon reaching equilibrium.

Model 2 – Concentration Effects in a Cell

$$Zn\,(s) + Cu^{2+}\,(aq) \leftrightarrow Zn^{2+}\,(aq) + Cu\,(s) \quad E^\circ = 1.100\text{ V}$$

Trial	Initial [Cu^{2+}] (M)	Initial [Zn^{2+}] (M)	Voltage (V)
1	1.00	0.25	1.116
2	1.00	0.50	1.108
3	1.00	0.75	1.103
4	1.00	1.00	1.100
5	0.75	1.00	1.097
6	0.50	1.00	1.092
7	0.25	1.00	1.084

8. In trials 1–7 in Model 2, what variables in the cell have been changed?

   The concentrations of zinc and copper ions in solution have been changed.

9. Consider the data in Model 2.
   a. Based on the principles of LeChâtelier, in which direction would you predict the reaction to shift when the concentration of copper ions is decreased?

   When the copper ion concentration is decreased, the reaction should shift left.

   b. What happens to the cell's potential (voltage) when the concentration of copper ions is decreased?

   The cell's potential decreases when the concentration of copper ions is decreased.

   c. Based on the principles of LeChâtelier, in which direction would you predict the reaction to shift when the concentration of zinc ions is decreased?

   When the zinc ion concentration is decreased, the reaction should shift right.

   d. What happens to the cell's potential when the concentration of zinc ions is decreased?

   The cell's potential increases when the concentration of zinc ions is decreased.

STOP

10. Predict the effect on the cell's potential when the concentration of copper ions is increased. Use LeChâtelier's Principle to justify your prediction.

    When the concentration of copper ions is increased, the reaction would shift right, which would increase the cell's potential.

11. Using the reaction in Model 1, estimate the conditions that would be required to achieve a cell potential of 1.00 V.

    The concentration of zinc ions would need to be higher than 1.75 M and the copper ion concentration would need to be less than 0.25 M. ***Note:*** *Students are not expected to use the Nernst equation here to find the exact concentrations. However, they should be able to follow the trend in the table and realize that there would need to be a significant change in concentration of the two ions in order to have a potential of 1.00 V.*

12. Consider the following reaction:

    $$F_2(g) + 2Cl^{1-}(aq) \leftrightarrow 2F^{1-}(aq) + Cl_2(g) \quad E^\circ = 1.51\ V$$

    a. Describe the conditions that would provide a voltage of 1.51 V.

    The chloride and fluoride ions would need to have a concentration of 1.00 M. The fluorine and chlorine gases would need to have a partial pressure of 1.00 atm.

    b. Identify two changes to the cell that would increase the potential of the cell.

    Possible answers include: increase the concentration of chloride ion, increase the partial pressure of fluorine gas, decrease the concentration of fluoride ion, decrease the partial pressure of chlorine gas.

    c. Identify two changes to the cell that would decrease the potential of the cell.

    Possible answers include: decrease the concentration of chloride ion, decrease the partial pressure of fluorine gas, increase the concentration of fluoride ion, increase the partial pressure of chlorine gas.

STOP

Extension Questions

Model 3 – Chromium and Zinc

$$3Zn\,(s) + 2Cr^{3+}\,(aq) \leftrightarrow 2Cr\,(s) + 3Zn^{2+}\,(aq) \quad E^\circ = 0.020\text{ V}$$

Trial	Initial [Cr^{3+}] (M)	Initial [Zn^{2+}] (M)	Voltage (V)
1	1.00×10^{-3}	1.00	–0.034
2	1.00×10^{-2}	1.00	–0.016
3	1.00×10^{-1}	1.00	0.002
4	1.00	1.00	0.020
5	1.00	1.00×10^{-1}	0.047
6	1.00	1.00×10^{-2}	0.074
7	1.00	1.00×10^{-3}	0.101

13. Under standard conditions, is the reaction in Model 3 spontaneous? Justify your answer.

The standard cell potential for the reaction is positive, so under standard conditions, it is spontaneous.

14. Describe a set of estimated conditions that would allow the reaction in Model 3 to be at equilibrium.

The cell potential would reach zero at equilibrium. In one possible set of conditions, the concentration of zinc ions would be 1.00 M and the concentration of chromium ions would be between 0.0100 M and 0.100 M.

15. According to Model 3, is it possible to make the reaction in Model 3 nonspontaneous? If yes, what was done to make this happen?

Yes, the cell's potential became negative (nonspontaneous) when the concentration of chromium ions was decreased.

16. Are the data in Model 3 consistent with LeChâtelier's principle? Justify your reasoning.

When the concentration of chromium ions is decreased, the reaction will shift to the left. If it shifts sufficiently, it could cause the reaction to no longer be spontaneous and begin to require voltage.

Teacher Resources – Electrochemical Cell Voltage

Learning Objectives

1. Predict qualitatively the change in voltage of a cell as concentrations or partial pressures of gases are increased or decreased using LeChâtelier's Principle.
2. Explain why the voltage of an electrochemical cell is not constant over time.

Prerequisites

1. Students should be able to label a drawing of an electrolytic or galvanic cell with the identity of the electrodes and contents of the cell when given a chemical reaction or description of the cell.
2. Students should be able to calculate the standard cell potential for an electrochemical cell and state the conditions in the cell that are required for that voltage to be delivered.
3. Students should understand that the voltage of an electrochemical cell is zero when the cell is at equilibrium.
4. Students should be able to predict the spontaneity of an electrochemical cell based on its standard cell potential—positive is spontaneous in the forward direction.
5. Students should be able to use LeChâtelier's Principle to predict shifts in chemical reactions when concentrations of solutions or partial pressures of gases change.

Assessment Questions

1. A student connects a battery to a voltmeter. The meter reads 1.34 V. The battery is then placed in a toy and used for several hours. What is the voltmeter likely to read when the battery is checked again?

   a. 1.34 V

   b. Less than 1.34 V

   c. More than 1.34 V

   d. The answer depends on the conditions of use.

2. Consider the below electrochemical cell at standard conditions. Which of the following changes would result in a voltage larger than 1.29 V?

   $$4MnO_4^{1-}(aq) + 4H^+(aq) \leftrightarrow 4MnO_2(s) + 3O_2(g) + 2H_2O \quad E° = 1.29\text{ V}$$

   a. Increase the partial pressure of oxygen gas.

   b. Increase the mass of solid manganese(IV) oxide present.

   c. Increase the pH.

   d. Increase the concentration of potassium permanganate.

3. Design an experiment using the idea of LeChâtelier's Principle and the change in cell potential of an electrochemical cell to determine if the following redox reaction is endothermic or exothermic.

$$\text{Zn (s)} + \text{Cu}^{2+}\text{(aq)} \leftrightarrow \text{Zn}^{2+}\text{(aq)} + \text{Cu (s)} \leftrightarrow \quad E^\circ = 1.100\text{ V}$$

Assessment Target Responses

1. *b*
2. *d*
3. *Set up the electrochemical cell several times using the same concentrations, but run it at different ambient temperatures. If the voltage increases when the temperature increases, then the reaction is endothermic. LeChâtelier's Principle predicts that an endothermic reaction will shift to the right when temperatures increase. If the voltage decreases when the temperature increases, then the reaction is exothermic. LeChâtelier's Principle predicts that an exothermic reaction will shift to the left when temperatures increase.*

Teacher Tips

- This activity does not introduce the Nernst equation for predicting the potential of a cell at non-standard concentrations. However, the values given in the Models of this activity were derived by the Nernst equation. If you have time, and wish to extend your students' understanding of this concept, you may introduce the Nernst equation following this activity.
- One major misconception with electrochemistry is the difference between E° and E = 0 V. This activity asks students to grapple with this misconception several times. It is important to note that E° is an arbitrary reference point that was decided upon in order to tabulate standard values. Our chemistry forefathers determined these values where concentrations were 1.00 M and partial pressures were 1.00 atm would be the most important. The conditions under which the reaction reaches equilibrium are not arbitrary however. They are a property of the substances involved.

Alignment with the AP Chemistry Framework

- **Essential Knowledge 3.C.3:** Electrochemistry shows the interconversion between chemical and electrical energy in galvanic and electrolytic cells.

  Learning Objective 3.12 The student can make qualitative or quantitative predictions about galvanic or electrolytic reactions based on half-cell reactions and potentials and/or Faraday's laws.

Faraday's Law

How can one predict the amount of product made in an electrolytic reaction?

Why?

In an electrolytic reaction, an electrical current is used to run a nonspontaneous redox reaction. This might be separating a metal from molten alloy or electroplating an object submersed in a metal cation solution. It may even be the electrolysis of water to collect oxygen and hydrogen gas. In any case, it is helpful to know how long the reaction will need to run to get the desired amount of product.

Model 1 – Collecting Pure Metal from Alloy

Experiment A

Trial	Run Time (hrs)	Current (Amperes)	Mass Ag Collected (g)	Moles Ag Collected
1	1.00	2.00	8.05	*0.075*
2	2.00	2.00	16.10	*0.149*
3	3.00	2.00	24.15	*0.224*
4	4.00	2.00	32.20	*0.299*
5	5.00	2.00	40.25	*0.373*
6	6.00	2.00	48.30	*0.448*

Experiment B

Trial	Run Time (hrs)	Current (Amperes)	Mass Na Collected (g)	Moles Na Collected
1	1.00	2.00	1.72	*0.075*
2	2.00	2.00	3.43	*0.149*
3	3.00	2.00	5.15	*0.224*
4	4.00	2.00	6.86	*0.299*
5	5.00	2.00	8.58	*0.373*
6	6.00	2.00	10.29	*0.448*

1. Model 1 shows data collected from two experiments where electric current was run through molten alloy containing the desired metal.

   a. Will the desired metal be collected at the anode or the cathode of the cell?

   The desired metal will be collected at the cathode.

   b. Write the half reaction that occurs as the metals are collected on the electrode.

   Experiment A electrode: $Ag^{1+} + e^- \rightarrow Ag(s)$

   Experiment B electrode: $Na^{1+} + e^- \rightarrow Na(s)$

2. Consider Experiment A of Model 1.

   a. Identify each of the following variables:

Independent	Dependent	Controlled
The time the cell is run.	*Mass of Ag collected.*	*Current of the cell.*

   b. Describe the relationship between the independent and dependent variable in this experiment. Linear? Inverse? Exponential? Logarithmic? Justify your answer.

   The relationship is a direct linear proportion. The slope of the line graphed would be constant. When another hour is added, an additional 8.05 g of silver is collected.

3. When the time and electrical current were identical in Experiments A and B, was the same mass of metal collected? Support your answer with evidence from Model 1.

   No, much less sodium is collected compared to silver with the same conditions of time and current. Trial 2 of experiment A yielded 16.10 g of silver while trial 2 of experiment B yielded only 3.43 g of sodium.

4. For each trial of Experiments A and B, calculate the moles of metal collected. Add these data points to Model 1 by adding a column to each of the tables. Divide the work among group members.

   See Model 1.

5. When the time and electrical current were identical in Experiments A and B, was the same amount of metal, in moles, collected? Support your answer with evidence from Model 1.

   Yes, when the conditions in the two experiments are identical, the same amount of metal, in moles, is collected. In trial 1 of both experiments, 0.075 moles of metal are collected.

Model 2 – A New Variable

Experiment C

Trial	Run Time (hrs)	Current (Amperes)	Ag Collected (mole)
1	1.00	1.00	0.037
2	1.00	2.00	0.075
3	1.00	3.00	0.112
4	1.00	4.00	0.149
5	1.00	5.00	0.187
6	1.00	6.00	0.224

6. Consider Experiment C of Model 2.

   a. Identify each of the following variables.

Independent	Dependent	Controlled
The current of the cell.	*The moles of Ag collected.*	*The time the cell is run.*

b. Describe the relationship between the independent and dependent variable in this experiment. Linear? Inverse? Exponential? Logarithmic? Justify your answer.

Current and moles of Ag collected have a direct linear relationship. The slope of the line would be constant at 0.038 mole/hour. For each additional Ampere, 0.038 mole of additional Ag are collected per hour.

7. Did any of the trials in Experiment C result in the same number of moles of metal being collected as that in Experiments A and B? If yes, list the time and current conditions for those that produced the same amounts of metal.

Yes, 2.00 hours at 2.00 Amperes yields the same moles of metal as 1.00 hour at 4.00 Amperes, and 3.00 hours at 2.00 Amperes yields the same moles of metal as 1.00 hour at 6.00 Amperes.

Read This!

Electrical current, a measure of the rate of electrons moving through a wire, can be thought of as water in a river passing a defined point. Electrical current is measured in Amperes. One amp is equal to one coulomb (unit of charge) per second. More coulombs (charge) will therefore move through a wire in an hour than in a minute at a given current. Similarly, more river water will move past a bridge in an hour than in a minute at a given current. As the magnitude of the current increases, more water (or charge) will pass a bridge (or move through a circuit) than at smaller currents in a given time span.

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8. Discuss with your group how the total charge might be calculated for each of the trials in Experiment C. Propose an equation for finding total charge of an electrolytic cell using the variables t for time, q for charge and I for current. *Hint:* Consider the base units of a Coulomb.

Current (in Amperes) × *time (in seconds)* = *charge (in Coulombs)*

$I \times t = q$

9. Do the trials in Experiments A and C that produced the same number of moles of metal have the same total charge?

Yes.

2.00 hours × *3600 sec/hr* × *2.00 C/s* = *14400 C*

1.00 hour × *3600 sec/hr* × *4.00 C/s* = *14400 C*

10. The experiment was done two more times:

Experiment D

Trial	Run Time (hrs)	Current (Amperes)	Moles Zn
1	1.00	2.00	0.037
2	2.00	2.00	0.075
3	3.00	2.00	0.112
4	4.00	2.00	0.149
5	5.00	2.00	0.187

Experiment E

Trial	Run Time (hrs)	Current (Amperes)	Moles Al
1	1.00	2.00	0.025
2	2.00	2.00	0.050
3	3.00	2.00	0.075
4	4.00	2.00	0.100
5	5.00	2.00	0.124

a. Write the half reaction that occurs at the electrode as these metals are collected.

Experiment D electrode: $Zn^{2+} + 2e^- \rightarrow Zn(s)$

Experiment E electrode: $Al^{3+} + 3e^- \rightarrow Al(s)$

b. Compare the moles of metal collected in Experiments D and E with the moles of metal collected in Experiments A and B under the same conditions of time and electrical current. Was the same number of moles of metal collected when conditions were equal? Justify your answer with data from the four experiments.

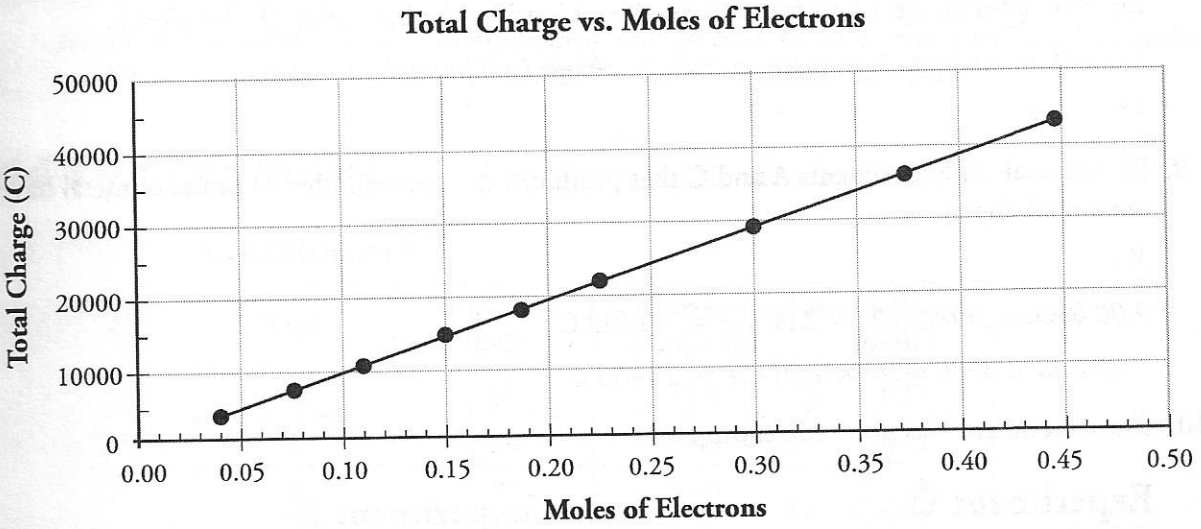
No, each of these experiments yielded less metal than Experiments A and B under the same conditions. The results of trial 1 in all four experiments have the same conditions of time and current, but in Experiments A and B, 0.075 mole of metal was produced. In Experiment D, only 0.037 mole was produced, and in Experiment E, only 0.25 mole of metal was produced.

11. Consider the number of electrons that are needed to reduce the molten ions in Experiments A–E to neutral atoms. Explain why the trials which have the same amount of total charge going through the cell produce different numbers of moles of metal when the charges on the ions are different.

When the charge on the ion is larger, it takes more electrons to reduce the ion. Therefore, the same charge results in fewer solid atoms being formed.

STOP

Model 3 – Faraday's Constant



12. Calculate the total charge for each of the trials in Experiments A and C. Graph the data from Experiments A and C in Model 3.

See Model 3.

13. Calculate the slope of the trend line for the graph in Model 3, including units. This ratio of total charge to moles of electrons is called **Faraday's constant**.

The slope is 96485 C/mole e⁻.

14. How many moles of electrons would be moved through the electrolytic cell if it ran for 45.0 minutes at a constant current of 3.85 Amperes?

$$\frac{(45.0\ \mathit{min})(60\ \mathit{s/min})(3.85\ \mathit{C/s})}{96485\ \mathit{C/mole}\ e^-} = 0.108\ \mathit{mole}\ e^-$$

15. How many moles of solid copper could be produced by electrolysis of molten $CuSO_4$ under the conditions in Question 14?

$$0.108\ \mathit{mole}\ e^- \times \frac{1\ \mathit{mole\ Cu}}{2\ \mathit{moles}\ e^-} = 0.0540\ \mathit{mole\ Cu}$$

16. Molten aluminum hydroxide is electrolyzed for 8.00 hours at 4.27 Amperes. Calculate the mass of aluminum metal that will be produced.

$$\left(\frac{(8.00\ \mathit{hr})\left(\frac{3600\ s}{1.00\ \mathit{hr}}\right)(4.27\ \mathit{amp})}{96485\ \mathit{C/mole}\ e^-}\right)\left(\frac{1\ \mathit{mole\ Al}}{3\ \mathit{moles}\ e^-}\right)\left(\frac{26.982\ g}{1\ \mathit{mole\ Al}}\right) = 11.5\ g\ \mathit{Al}$$

Extension Questions

Model 4 – Electrolysis of Aqueous Solutions

Experiment F

Trial	[$AgNO_3$] (M)	Run Time (hrs)	Current (Amperes)	Ag Collected (mole)
1	0.20	1.00	3.00	0.11
2	0.40	1.00	3.00	0.11
3	0.60	1.00	3.00	0.11
4	0.80	1.00	3.00	0.11
5	1.00	1.00	3.00	0.11

17. Consider Experiment F in Model 4.

    a. Identify each of the following variables:

Independent	Dependent	Controlled
The [Ag^{1+}] in solution.	*The moles of Ag collected.*	*Time and current.*

    b. Describe the relationship between the independent and dependent variable in this experiment. Linear? Inverse? Exponential? Logarithmic? Justify your answer.

    The concentration of silver ions in the solution has no effect on the amount of solid metal collected in the cell.

18. Propose an atomic level explanation for the data in Experiment F.

    The amount of silver collected is not dependent on what is in solution, but rather the availability of electrons that are being added to the silver ions at the cathode. The current and time determine the availability of the electrons and since they were constant, the amount of silver collected was constant.

19. What is the minimum voltage needed for Trial 5 of Experiment F to work?

    The half-cell reactions will be:

    $Ag^{1+}(aq) + e^- \rightarrow Ag(s)$ $\qquad E° = 0.80\ V$

    $2H_2O \rightarrow + O_2(g) + 4H^+(aq) + 4e^-$ $\qquad E° = 1.23\ V$

    Therefore the total cell voltage must be $E°\ cell = -0.43\ V$.

    For the reaction to work, the cell voltage must be exceeded.

Teacher Resources – Faraday's Law

Learning Objectives

1. Describe qualitatively how the time, current and charge on the cation affect the productivity of an electrolytic cell.
2. Calculate the moles of product for an electrolytic cell given the half reactions, time and current of the cell.

Prerequisites

1. Students need to be able to identify the independent, dependent and controlled variables when given a set of data from an experiment.
2. Students need to know that electrolytic cells are nonspontaneous.
3. Students need to be able to identify the reaction that would take place at the cathode and anode of an electrolytic cell given the bulk contents of the cell (molten alloy or aqueous solution).
4. Students should know that electrical current is a flow of electrons.

Assessment Questions

1. Which of the following variables in an electrolytic cell will determine the amount of product produced?

   I. Time the cell is run

   II. Current

   III. Voltage of the cell

   IV. Surface area of the electrodes

   a. I only

   b. III only

   c. I and II

   d. III and IV

2. Several electrolytic cells were run under the following conditions. Which cell will produce the most solid metal product?

   a. Molten copper(II) nitrate is electrolyzed for 2.00 hours at 3.00 Amperes.

   b. Molten copper(II) nitrate is electrolyzed for 2.00 hours at 4.00 Amperes.

   c. Molten silver nitrate is electrolyzed for 2.00 hours at 4.00 Amperes.

   d. Molten aluminum hydroxide is electrolyzed for 2.00 hours at 4.00 Amperes.

3. Molten zinc hydroxide is electrolyzed for 15.00 hours at 3.85 Amperes. Calculate the mass of zinc metal that will be produced.

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Assessment Target Responses

1. *c*
2. *c*
3. *70.4 g Zn*

Teacher Tip

- It is important to explain to students that the current of a cell is almost never constant over several hours. The situations in this activity are idealized. Typically, as the cell runs the current will drop. This can be adjusted by changing the voltage, but there will still be slight fluctuations that are not ideal.

Alignment with AP Chemistry Framework

- **Essential Knowledge 3.C.3:** Electrochemistry shows the interconversion between chemical and electrical energy in galvanic and electrolytic cells.

  Learning Objective 3.12 The student can make qualitative or quantitative predictions about galvanic or electrolytic reactions based on half-cell reactions and potentials and/or Faraday's laws.

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